PB80-196785

Analysis of Houston Aerosol Samples by GC/MS (Gas Chromatography-Mass Spectrometry) Methods

Arizona State Univ., Tempe
Dept. of Chemistry

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

Apr 80

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-80-071		PB 80 196785

4. TITLE AND SUBTITLE	5. REPORT DATE
ANALYSIS OF HOUSTON AEROSOL SAMPLES BY GC/MS METHODS Final Report	April 1980 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
F. W. Karesek and M. L. Parsons	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Arizona State University Department of Chemistry Tempe, Arizona 85281	1AA603 AH-16(FY-78) 11. CONTRACT/GRANT NO. 68-02-2961
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Sciences and Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	Final 9/78 - 6/79 14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

An analysis procedure developed to give a qualitative and quantitative analysis for organic compounds adsorbed on aerosols collected by Hi-Vol filters was adapted and applied to a similar analysis of aerosols collected by dichotomous filters. Analysis was conducted for five dichotomous samples and two Hi-Vol samples collected in the Houston study. Estimated concentration levels for dichotomous filters of 0.1 to 20 ng/m^3 were reported for the 27 organic compounds searched. Compounds detected included carboxylic acid esters, phthalates, n-alkanes and polycyclic aromatic hydrocarbons. The quantities observed in the samples were near the detection limits of the GC/MS-SIM analysis, and blanks of the instrumental system, solvent, procedure and filter elements were necessary to identify artifacts introduced. Filter and solvent blanks contained compounds in the same or higher quantity ranges as did the filter samples, indicating the teflon elements of the dichotomous filters were not cleaned sufficiently prior to use.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Air pollution *Aerosols *Organic compounds *Quantitative analysis *Qualitative analysis *Gas chromatography *Mass spectrometry		13B 07D 07C 14B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

United States
Environmental Protection
Agency

Environmental Sciences Research
Laboratory
Research Triangle Park NC 27711

EPA-600/2-80-071
April 1980

Research and Development

PB80-196785

EPA

Analysis of Houston Aerosol Samples by GC/MS Methods

Final Report

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/2-80-071
April 1980

ANALYSIS OF HOUSTON AEROSOL SAMPLES BY GC/MS METHODS

Final Report

by

F. W. Karasek and M. L. Parsons
Arizona State University
Department of Chemistry
Tempe, Arizona 85281

Contract No. 68-02-2961

Project Officer

Kenneth J. Krost
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratories
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

This report has been reviewed by the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

An analysis procedure developed to give a qualitative and quantitative analysis for organic compounds adsorbed on aerosols collected by Hi-Vol filters was adapted and applied to a similar analysis of aerosols collected by dichotomous filters. The procedure involves a 12 hour Soxhlet extraction with methanol, concentration of extract by a factor of 200 to 2000 by rotary evaporation under aspirator vacuum and analysis by GC and GC/MS. Analysis was conducted for five dichotomous samples and two Hi-Vol samples collected in the Houston study. Estimated concentration levels for dichotomous filters of 0.1 to 20 ng/m^3 were reported for the 27 organic compounds searched. Compounds detected included carboxylic acid esters, phthalates, n-alkanes and polycyclic aromatic hydrocarbons. Because of the uncertainties, low level of compounds and need for multiple analyses involved, concentrates were not reduced below 50 µl volumes. The quantities observed in the samples were near the detection limits of the GC/MS-SIM analysis, and blanks of the instrumental system, solvent, procedure and filter elements were necessary to identify artifacts introduced. Filter and solvent blanks contained compounds in the same or higher quantity ranges as did the filter samples, indicating the teflon elements of the dichotomous filters were not cleaned sufficiently prior to use. Results from analysis of one-quarter portions of the Hi-Vol filter samples showed a very light loading of organic compounds, giving values of 1 to 17 ng/m^3 for the same types of compounds as found in the dichotomous filters. Duplicate analyses of these samples showed a high degree of qualitative reproducibility for the procedure. While these samples contained a higher concentration of many organic compounds by a factor of 5 to 10 than the dichotomous samples, they did not appear to be typical of Hi-Vols from industrialized areas.

CONTENTS

Abstract..... iii

Figures..... vi

Tables..... vii

Acknowledgement..... viii

1. Introduction..... 1

2. Conclusions..... 4

3. Experimental Procedures..... 5

Sample History..... 5
Glassware Cleaning..... 7
Dichotomous Filter Extraction..... 7
Hi-Volume Filter Extraction..... 9
Analysis by Gas Chromatography..... 9
Analysis by Gas Chromatography/Mass Spectrometry..... 13
Solvent Study..... 16

4. Results and Discussion - Part I..... 19

5. Results and Discussion - Part II..... 38

References..... 48

Appendix - GC/MS Data..... 49

Preceding page blank

FIGURES

Number		Page
1	GCPLOT of analysis of methanol solvents concentrated as procedure blank	21
2	SIM plot of PG-2 analysis	24
3	GCPLOT of SIM data for dichotomous filters	29
4	SIM plot of system blank for 3F-016	30
5	SIM plot of 3F-016 analysis	32
6	SIM plot of GC CALIBRATION MIXTURE analysis for dichotomous samples	34
7	GCPLOT of duplicate Hi-Vol filter samples and blanks	36
8	GCPLOT of dichotomous filter samples and solvent blank	37
9	SIM plot of Hi-Vol sample 0052-1	39
10	SIM plot of Hi-Vol sample 0052-2	40
11	SIM plot of Hi-Vol sample 0086-1	41
12	SIM plot of Hi-Vol sample 0086-2	42
13	GCPLOT of SIM data of Hi-Vol samples 0052-1 and 0086-1 for components identified in Table 11	45
14	Plots from Dual-Mode analysis of 0052-1	46
15	Plots from Dual-Mode analysis of 0086-1	47

TABLES

Number		Page
1	Sample History	6
2	Steps in Glassware Cleaning Procedure	8
3	Steps in Dichotomous Filter Extraction and Analysis Procedure	10
4	Steps in Hi-Vol Filter Extraction and Analysis Procedure	11
5	Comparisons of Extraction Procedure - ASU	12
6	GC Conditions - ASU (Dichotomous & Hi-Vol Filter Analysis)	14
7	Conditions for Analysis (GC/MS)(UW)	15
8	Ions Monitored in SIM and GC/MS Analysis	17
9	SIM Data for Dichotomous Filters using PG solvent	22
10	Concentrations (ng/m^3) of Organic Compounds in Dichotomous Filter Extracts	27
11	SIM Quantitation of Hi-Vol Samples 0052-1 and 0086-1	44

ACKNOWLEDGEMENTS

We wish to acknowledge the careful and extensive work done on this very difficult analytical problem by W. D. Bowers of ASU and G. A. Eiceman and R. E. Clement of UW.

SECTION 1

INTRODUCTION

Sampling of aerosols by drawing large amounts of air through a fiber glass filter element has been an established procedure since 1967 (1). The apparatus used routinely for such sampling (Hi-Vol), however, gives no information concerning particle size distribution. Such data are important for health studies since only the very fine particles can penetrate deep into the human respiratory system (2). Particle size information can be obtained by sampling air with the use of a cascade impaction sampling device (3,4). This technique can be used to collect particulate matter in several size ranges. Van Cauwenberghe and co-workers (3,4) have combined the use of a 6-stage cascade impactor for sampling with the technique of gas chromatography-mass spectrometry (GC/MS) for the comparison of organic pollutant levels on various particle sizes of aerosols. Organic compounds of low volatility were found to be primarily associated with the small particle sizes of less than 3 μm diameters.

For most studies, extensive fractionation of particles into many size-distribution categories is not necessary. Liu has reported that the volume of aerosol in ambient air has a bimodal distribution with a relative minimum at particle diameters of about 2 μm (2). Also, Harris and Lippmann have established that particles smaller than 3.5 μm diameter can penetrate deeply into the human respiratory system, while larger particles are trapped in the upper respiratory system, while larger particles are trapped in the upper respiratory passages (5). In addition, separation of aerosol into many sizes may require lengthy sampling periods to obtain the quantity of sample needed to perform organic and inorganic analyses.

For most studies, therefore, separation of aerosol into two particle size ranges would seem to be sufficient to develop useful information.

Forley has described a single stage, variable slit impactor which is capable of determining entire particle-size distributions, or fractionating particles into two size classes for mass or chemical analysis (6). Stevens used a dichotomous sampler to collect fine (<3.5 μm diameter) and coarse (> 3.5 μm) particles for determination of atmospheric sulphates (7). More than 70 percent of the sulfur was determined to be present in the fine particle fraction for at least 90% of the samples analyzed. Use of the dichotomous sampler is particularly suited for inorganic analysis by techniques such as X-ray Fluorescence (XRF) (8,9,10). By using suitable filter elements, aerosols may be analyzed by XRF directly after sampling, with no additional sample treatment necessary. Use of the dichotomous sampler provides a reasonable compromise between fractionation of atmospheric aerosols by size for health studies and quantity of particulate collected for analytical purposes.

Little work has been done to date to provide for the analysis of organic compounds adsorbed onto particulate matter collected by dichotomous samplers. Because of the suspected carcinogenic effects of some organic compounds, notably the polynuclear aromatic hydrocarbons (PAHs), it is important to know the distribution of these compounds between respirable and non-respirable fractions of airborne particluate matter.

In methods reported for organic analysis, adsorbed organic constituents are solvent extracted from particulates on the filter surface, and analyzed by GC and GC/MS. Methods of extraction vary greatly between laboratories, some of which require a great deal of sample handling. Steps involved in sample preparation may include extraction, sample clean-up, preseparation of particular components of interest or separation into basic and acidic fractions.

Recently, a simplified, effective analytical procedure has been developed to give a qualitative and quantitative analysis of organics compounds adsorbed onto aerosols collected by Hi-Vol Filtration (11). This procedure involves a 2 to 12 hour Soxhlet extraction with methanol, concentration by a factor of 200 by rotary evaporation under aspirator vacuum, and analysis by GC and GC/MS, with no further sample treatment. Data is processed and presented via specialized computer programs in a format permitting easy sample comparisons. Elimination of extra treatment steps greatly speeds

analysis time and reduces chances for sample losses. For samples with very low organic loadings, GC/MS analysis using the technique of Selected Ion Monitoring (SIM) may be used to increase analytical sensitivity for compounds of interest. The study reported here was undertaken to evaluate the applicability of this rapid procedure, or some modification of it, for the analysis of organic compounds associated with aerosols collected by dichotomous filters.

SECTION 2

CONCLUSIONS

These results pertain specifically to the procedure and instrumental system used: namely, Soxhlet extraction with methanol, condensation, and GC, GC/MS analysis with instrumentation involving special Aue-type packed columns and a quadrupole mass spectrometer equipped with a membrane interface. Although several of the common compounds expected to be associated with these aerosol samples were detected, application of this analysis procedure gave inadequate results for routine analysis of dichotomous filter samples for organic content. This work showed the need for high solvent purity, careful determination of solvent, column, instrumental system and filter element blanks to separate artifacts introduced from compounds detected.

The need for a different approach to this analysis which minimizes the artifact introduction and increases the extraction efficiency and instrumental sensitivity is seen. An approach utilizing an inert, sealed extraction-condensation apparatus could permit a condensation increase by a factor of 5 and minimizes artifact introduction. If the extraction efficiency could be increased by a factor of 2 using ultrasonic techniques and another factor of 10 increase in sensitivity achieved by modification of the GC/MS operating conditions, an overall increase in detectability of a factor of 100 would be achievable. This higher detectability-to-background ratio would be able to provide useful information on organic content.

SECTION 3

EXPERIMENTAL PROCEDURES

SAMPLE HISTORY

Dichotomous Filters

Ten dichotomous filter samples were taken from sites in Houston, Texas by the Radian Corporation, the agent responsible for collecting and shipping filter samples. The ten samples, 3F-017, 3C-017; 3F-031, 3C-031; 3F-028, 3C-028; 3F-016, 3C-016; and 3F-032, 3C-032 and two blanks 3F-033, 3C-033 were received on October 18, 1978 and transferred from the shipping containers, where filters were cooled with dry ice, directly to a freezer (-19°C) until analyzed. The filters were inspected visually and filters 3F-017 and 3F-031, which appeared most heavily loaded with particulate matter, were extracted using the Soxhlet apparatus method (1,2) and pesticide grade (PG) methanol (Fisher Scientific Company, Fairlawn, NJ). They were extracted with PG methanol since reported levels of organic impurities in this solvent were low.

It was later found that the "distilled-in-glass" BJ methanol (Burdick and Jackson, Muskegan, MI) contained a lower level of impurities. The remaining filters and filter blanks were then extracted by the Soxhlet apparatus method using the BJ methanol solvent. Table 1 lists the history of the samples analyzed.

High-Volume Filters

High-Volume filter [Hi-Vol] samples 0052 and 0086 were received February 5, 1979 in sealed glass tubes packaged in dry ice. The tubes were transferred directly to a freezer (-19°C) until analyzed. A one-quarter portion of each filter was extracted using a soxhlet apparatus and the BJ methanol. Following extraction, samples were analyzed by gas chromatography

TABLE 1 HISTORY OF SAMPLES ANALYZED

Sample	Sample	Date and Time Sample Collected	Date Sample Received ASU	Date Extracted ASU	Date of Analysis GC(ASU)	GC/MS(UW)	GC/MS(UW) SIMS
3F-017	Houston Site 19	9-28-78:0608 to 9-28-78:1808	10-18-78	11-23-78	11-23-78	11-28-78	11-28-78
3F-031	Houston Site 21	10-9-78:0600 to 10-9-78:1800	10-18-78	11-21-78	11-22-78	11-28-78	11-28-78
3F-028	Houston Site 17	10-6-78:0600 to 10-6-78:1852	10-18-78	1-28-79	2-2-79	2-22-79	2-22-79
3F-016	Houston Site 19	9-27-78:1808 to 9-28-78:0608	10-18-78	1-28-79	2-3-79	2-23-79	2-23-79
3F-032	Houston Site 21	10-10-78:0600 to 10-10-78:1800	10-18-78	1-29-79	1-30-79	2-23-79	2-23-79
3C-031	Houston Site 21	10-9-78:0600 to 10-9-78:1800	10-18-78	1-29-79	1-30-79	2-23-79	2-23-79
3F-033 Blank	-	-	10-18-78	1-31-79	2-2-79	2-23-79	2-23-79
3C-033 Blank	-	-	10-18-78	1-31-79	2-1-79	2-23-79	2-23-79
0052* Hi-Vol	unknown	unknown	2-5-79	2-20-79	2-21-79	3-27-79	4-02-79
0086* Hi-Vol	Houston Site 1	10-3-78:0610 to 10-3-78:1800	2-5-79	2-20-79	2-24-79	3-27-79	4-02-79
0085 Hi-Vol Blank	-	-	5-8-79	5-13-79	5-14-79	-	-

* These filter elements were not cleaned for organic analysis and will contain high and variable organic background.

at Arizona State University (ASU) and sent to the University of Waterloo (UW) for analysis by gas chromatography/mass spectrometry and Selected Ion Monitoring (SIM). A Hi-Vol filter blank, sample 0085, supplied by the contractor at a later date was extracted and analyzed by the same procedure.

GLASSWARE CLEANING

All glassware was washed with an aqueous solution of Alconox detergent (Alconox, Inc., New York, NY), thoroughly rinsed with analytical reagent (AR) grade methanol (Fisher Scientific Co., Fairlawn, NJ), rinsed with BJ grade methanol and dried at 115°C for several hours. Soxhlet glassware was cooled, assembled and operated with 100 mls of methanol for 12 hours as a final cleaning procedure. Following this procedure the 100 mls of BJ methanol were discarded and the glassware was used immediately. After drying, sample vials were boiled in BJ methanol for 5 hours and used. The cleaning procedure is outlined in Table 2.

DICHOTOMOUS FILTER EXTRACTION PROCEDURE

Dichotomous filter samples were removed from the freezer using Teflon forceps and the filters separated from the plastic holders with a razor blade and Teflon forceps. The Teflon filters were not in contact with any object that was not cleaned and also methanol rinsed. Each filter was placed in a 80 mm high x 25 mm I.D. coarse fritted glass extraction thimble and the thimble inserted into a 30 mm I.D. Pyrex Soxhlet tube (Fisher Scientific Co., Fairlawn, NJ). The entire extraction apparatus filled with 100 milliliters of BJ methanol was assembled. Ground glass joint greases were not used in an attempt to avoid introducing contaminants. Filters were continuously extracted for 12 hours in the Soxhlet apparatus.

After cooling to room temperature, the 100 milliliter extract was condensed to approximately 5 milliliters using a rotary flash evaporator (Buchler, Fort Lee, NJ). After quantitative transfer to a 10 milliliter round bottom flask with a clean disposable pipet, the extract was further reduced in volume to 0.5 milliliters. The extract was quantitatively transferred to a 1 milliliter reacti-vial (Altech Associates, Arlington Heights, IL) sealed with screw cap and Teflon liners. A stream of ultra pure (99.9%) nitrogen (Liquid Air, Phoenix, AZ), directed across the mouth of the

TABLE 2

STEPS IN GLASSWARE CLEANING PROCEDURE

I. Detergent wash

a) Aqueous solution of Alconox detergent rinse
b) Distilled water rinse
c) AR grade methanol rinse
d) BJ methanol rinse

II. Dry in oven @ 115°C - two hours

SOXHLET APPARATUS	SAMPLES VIALS
III. Soxhlet glassware assembled & operated 12 hours as a pre-rinse with 100 ml of BJ methanol	III. Boiled in BJ methanol for 5 hours
IV. [After prerinse completed] Methanol discarded and glassware used immediately	IV. Ready for use

sample vial was used to reduce the volume of the extract to 50 microliters. Table 3 outlines steps in the extraction procedure.

HIGH-VOLUME FILTER EXTRACTION PROCEDURE

The sealed glass tube containing the Hi-Vol filter was removed from the freezer and allowed to reach room temperature. The tube was opened at one end and the foil-wrapped filter removed. The foil was separated from the filter using Teflon forceps and the filter cut in half. One half was re-wrapped in the foil, inserted into the tube and the tube resealed. The tube was returned to the freezer (-19°C). The remaining half was cut into halves (a quarter of the original filter). Quarter filters were cut into 1 cm squares, placed in the glass extraction thimble and continuously extracted with 100 ml of distilled in glass methanol in the Soxhlet apparatus for 12 hours.

The methanol extract, after cooling, was condensed in volume to 5 milliliters using the rotary flash evaporator. The extract was quantitatively transferred to a round bottom flask and further condensed to approximately 0.3 ml, and transferred to a sample reacti-vial and was adjusted to a final volume of 0.5 milliliters.

Following gas chromatographic analysis, 0.2 milliliters of the final concentrate were transferred to 0.1 milliliter reacti-vial, and reduced in volume to 50 microliters using a stream of high purity nitrogen (Twin Cities Welding, Kitchener, Ontario) directed over the mouth of the reacti-vial. The more concentrated extract was used in GC/MS analysis. The remaining 0.3 milliliters was placed under refrigeration (2-5°C). Extraction procedures for Hi-Vol filters are given in Table 4.

A comparison of volume and concentration factors between dichotomous filter and Hi-Vol filter extraction procedures is listed in Table 5.

ANALYSIS BY GAS CHROMATOGRAPHY

All extracts were first analyzed on a 5830A Hewlett-Packard digital gas chromatograph employing a 2 meter x 2mm I.D. glass column containing Aue packing and equipped with a flame ionization detector. Aue packing consists of an ultra-thin film of Carbowax 20M which is physically bonded to Chromosorb W that has been exhaustively extracted with an aqueous hydrochloric acid

TABLE 3

STEPS IN THE DICHOTOMOUS FILTER EXTRACTION
AND ANALYSIS PROCEDURE

I. Soxhlet extraction for 12 hours with 100 ml BJ methanol

II. Condensation of extract to 50 µl
   a) 100 ml evaporated to ≈ 5 ml
   b) Transferred to 10 ml flask and evaporated to ≈ 0.5 ml
   c) Transferred to clean sample vial and evaporated to 50 µl with stream of ultra-pure N_2 gas purging across top of sample vial

III. GC analysis of final 50 µl extract
   a) Column blank
   b) Filter extract - 3 µl injection
   c) Hydrocarbon standard

IV. GC/MS analysis (Peakfinder)
   a) Column blank
   b) Methanol system blank
   c) Filter extract of 2-5 µl injections
   d) Calibration mixture

V. GC/MS analysis (SIM)
   a) Column blank
   b) Methanol system blank
   c) Filter extract of 2 to 5 µl
   d) Calibration mixture

(a) steps I to III conducted at ASU; steps IV and V at UW

TABLE 4

STEPS IN THE HIGH-VOLUME FILTER EXTRACTION
AND ANALYSIS PROCEDURE

I. Soxhlet extraction for 12 hours with 100 ml BJ methanol using 1/4 filter

II. Condensation of extract to 0.5 ml
   a) 100 ml evaporated to ≈ 5 ml
   b) Transferred to 10 ml flask and evaporated to ≈ 0.3 ml
   c) Transferred to sample vial and brought to final volume of 0.5 ml

III. GC analysis of 0.5 ml extract
   a) Column blank
   b) Filter extract 3 µl injection
   c) Hydrocarbon standard

IV. Further sample condensation
   a) 0.2 ml evaporated to 50 µl

V. GC/MS analysis (Peakfinder)
   a) Column blank
   b) Methanol system blank
   c) Filter extract - 3 µl injection
   d) Calibration mixture

VI. GC/MS - (SIM)
   a) Column blank
   b) Methanol system blank
   c) Filter extract - 3 µl injection
   d) Calibration mixture

(a) steps I to III conducted at ASU; steps IV to VI at UW

TABLE 5

COMPARISON OF EXTRACTION PROCEDURES - ASU

	Initial Extraction Solvent Volume (mL)	Final Sample Volume (μL)	Concentration Factor	Volume of Air Sampled (M^3)	Volume of Air per μL of Concentrated Extract
Soxhlet Extraction Dichotomous Filters	100	50	2000	12	0.24
Hi-Vol Filters (One-Fourth of Filter Extracted)	100	500	200	500	1.0

solution (12). The high efficiency of separation and the application of Aue packing for analysis of complex environmental samples has been demonstrated (11,13). In addition, Aue packing yields rapid and convenient analyses and exhibits low bleed properties making it suitable for application in GC/MS methods. Gas chromatographic conditions are listed in Table 6.

Column blanks were run before each sample to determine levels of artifacts introduced by the septum or column. Three microliters of the samples were then analyzed. A hydrocarbon standard was also analyzed following each sample and hydrocarbon retention times used to calculate retention indices under temperature programmed conditions (11). Retention indices were used in computer generated plots of peak area against retention index. These plots were developed at the University of Waterloo and make possible rapid and convenient comparisons of qualitative and quantitative distributions of organic compounds in complex mixutres (14). The plots, referred to as RIPLOTS, also can be generated using retention times and are then called GCPLOTS. A similarly equipped 5830A gas chromatograph was used at the University of Waterloo where the ASU GC operating conditions were duplicated.

ANALYSIS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Sample extracts were analyzed with a Hewlett-Packard 5992A GC/MS which was calculator controlled and equipped with single floppy disk, X-Y plotter, membrane separator and 2 or 2.7 meter x 2mm I.D. glass column containing Aue packing. Operating parameters for GC/MS system were optimized daily using a perfluorotributylamine standard and software supplied by the manufacturer (15). Extracts were analyzed using the GC/MS in both the scanning (Peakfinder, Dual-Mode) and Selected Ion Monitoring modes of operation. Operating conditions for the GC/MS analysis are given in Table 7.

Scanning Mode

During temperature programmed gas chromatographic analysis the mass spectrometer scanned continuously from m/e 500 to m/e 40 at a rate of 330 atomic mass units/second. Software supplied by the manufacturer (Peakfinder) stores mass spectra taken at the top of eluting peaks and stores the spectra on disc. An eluting peak is detected when a threshold value for total ion abundance is exceeded. A low threshold value was used for this study so

TABLE 6

GC CONDITIONS - ASU
(DICHOTOMOUS & HI-VOL FILTER ANALYSIS)

Temperature 1	80°C
Time 1	4 minutes
Temperature Program Rate	4°C/minute
Temperature 2	240°C
Time 2	30 minutes
Injection Port Temperature	240°C
Flame Ionization Detector	240°C
Temperature	240°C
Attenuation	8
Helium Carrier Flow Rate	30 ml/minute
Sample Size	3 µl
Column	2m x 2mm I.D. Glass
Packing	Aue Packing, 80/100 mesh

TABLE 7

CONDITIONS FOR ANALYSIS (GC/MS) (UW)

Temperature 1	90°C
Time 1	0 min
Rate	4°C/min
Temperature 2	250°C
Time 2	15 min
Injection Port Temperature	250°C
Helium Carrier Flow Rate	40 ml/min
Sample Size	2 to 5 µl
Column	2 or 2.7m x 2mm I.D. Glass
Packing	Aue Packing 80/100 mesh
Separator	Silicone Membrane
Ionization Source	Electron Impact
Mass Spectrometer Type	Quadrapole
Detector	Channeltron Electron Multiplier (EM)
EM Voltage	Autotune Value Used
Solvent Time Out	2.5 to 3 minutes
GC Peak Detect Threshold	200 to 1000
Mass Peak Detect Threshold	2000

spectra were saved from even minor components. Mass scans taken at the lowest abundance values between consecutive peaks were also saved as background. Each background spectrum was subtracted from its corresponding peak spectrum when the GC/MS run was terminated and this process provided spectra more suitable for interpretation.

A modified version of Peakfinder, called Dual-Mode, developed at the University of Waterloo, became available for use in March 1979 and was used in the analysis of the Hi-Vol samples [16]. The Dual-Mode software, in addition to saving mass spectra as in Peakfinder, is also capable of storing time/abundance data on disc for later generation of reconstructed gas chromatograms and as many as six mass chromatograms. Conditions for analysis were unchanged from those used in Peakfinder.

Selected Ion Monitoring (SIM)

The SIM mode of analysis allows consecutive sampling of as many as six ions which are pre-selected by the operator. During a GC run the abundance of a particular ion is measured for a specified dwell time before sampling the next ion. Dwell times used were 166 msec for all ions monitored by SIM. For each sample analyzed two separate SIM runs were made giving a total of 12 ions which were monitored. By knowing retention times of compounds associated with these ions, identifications can be made. The ions which were monitored are given in Table 8, along with the compounds or compound classes characteristic of these ions. Quantitation was provided by running a calibration mixture which contained normal hydrocarbons, phthalates, alcohols and selected polynuclear aromatic hydrocarbons (PAHs). Use of SIM allows detection of even minor components since sensitivity is greatly increased by dwelling on a particular ion for a long time period relative to the short dwell time of Peakfinder or Dual Mode.

Solvent Study

Since the pesticide grade methanol concentrate contained impurities of about the same quantities as the organic compounds extracted from the dichotomous filters, this seriously interferred with determination of compounds which were extracted from the dichotomous filter. It was known from work done at the University of Waterloo that the Burdick and Jackson methanol was quite

TABLE 8

IONS MONITORED IN SIM AND GC/MS ANALYSIS

Ion in m/e	Compound or Class
SIM	
43.1	n-Hydrocarbon series
57.1	n-Hydrocarbon series
60.1	n-Aliphatic acids, n-Hydrocarbon series
74.1	n-Methyl ester series
85.1	n-Hydrocarbons series
149.1	Phthalate esters
154.1	Biphenyl, Acenaphthene
163.1	Dimethyl Phthalate
166.1	Fluorene
178.1	Anthracene
202.1	Fluoranthene, Pyrene
228.1	Triphenylene, Chrysene, Benzo(a)-anthracene
252.1	Benzo[a]pyrene, Benzo[k]fluoranthene
Dual Mode GC/MS	
74.1	n-Methyl ester series
85.1	n-Hydrocarbon series
149.1	Phthalate esters
178.1	Anthracene
202.1	Fluoranthene, Pyrene
252.1	Benzo[a]pyrene, Benzo[k]fluoranthene

low in impurities. Therefore, a study to compare the impurity levels of various types of methanol was conducted to determine which methanol would be best to use for the extraction of the dichotomous filters. The three types of methanol investigated were analytical reagent (AR), pesticide grade (PG), and the "distilled in glass" (BJ).

The glassware was cleaned as in the general procedure. After the 12 hours of operation as a prerinse in BJ solvent, the used solvent was discarded and 100 mls of fresh BJ solvent was added to the apparatus. After the 12 hour extraction period, the solvent blank, BJ-1, was condensed down to fifty microliters as in the general procedure. This solvent blank was then analyzed by GC and GC/MS. A second solvent blank, BJ-2 was done by the same procedure with essentially the same results.

The AR and pesticide grade methanol were treated in the same manner and procedure as the BJ solvent. These solvent blanks were designated AR-1 and PG-1 representing the analytical reagent grade and pesticide grade methanol respectively.

SECTION 4

RESULTS AND DISCUSSION - PART I

GC/MS ANALYSIS DICHOTOMOUS FILTER ANALYSIS

Methanol extracts of dichotomous filters were found to contain 0.1 to 20 ng/m^3 per organic compound, with one compound, dibutyl phthalate, being present at 150 ng/m^3. Near 0.1 ng/m^3 the detection limits of SIM analysis are approached and stringent steps were required to identify sources of contamination and prevent loss of sample integrity during extraction, concentration, and analysis. Artifacts from the instrumentation are also possible at these very high levels of sensitivity and were monitored with system blanks. System blanks indicated that syringe and instrumental contamination was at or near the noise level of the instrument.

The dichotomous filter analysis can be divided into three phases. First, filters 3F-017 and 3F-031 were extracted with Pesticide Grade (PG) methanol and analyzed by GC/MS (Peakfinder Mode) and SIM. The results of these analyses indicated a solvent with far less impurities than present in the PG grade would be necessary to obtain useful results. Second, different grades of methanol, PG, AR and BJ were concentrated and analyzed by GC-FID. The AR grade methanol concentrate, which contained the most impurities, was analyzed by GC/MS. Finally, the remaining dichotomous filters were extracted with the BJ solvent, which had the least impurities, and the extracts analyzed using SIM.

Initial results from the GC/MS (Peakfinder Mode) analysis of filter 3C-031, which was extracted with BJ methanol and which contained the highest concentration of organic compounds, indicated that concentration levels for individual components were near or below detection levels. Therefore, all remaining dichotomous filters (extracted with BJ methanol) were analyzed by SIM which is a more sensitive technique than regular GC/MS analysis.

GC/MS (Peakfinder Mode)

Three filters 3F-017, 3F-031, and 3C-031 were analyzed using GC/MS (Peakfinder Mode). The first two filters were extracted with PG methanol, and showed 12 to 15 components. However, the PG methanol concentrate itself contained many of the same components which, if they had originated from a filter sample, would have shown an estimated equivalent concentration of 0.1 to 10 ng/m^3 per component. The GC/MS results from these three filters were inconclusive.

Three grades of methanol were then analyzed by GC to determine the contribution of organic compounds to filter extracts following volume reduction to 50 or 100 µl. Figure 1 is the GCPLOT from the chromatographic analysis of different methanol solvent concentrates. The major components found in PG solvent concentrate are methyl myristate, methyl palmitate, methyl stearate, diethyl phthalate and dioctyl phthalate. Since these components predominate in 3F-017 and 3F-031, it is difficult to determine the components which are contributed by the filter samples.

Figure 1 also clearly shows that BJ methanol contains the lowest levels of impurities and it was chosen for extraction of 3C-031 and all other filters.

Analysis of 3C-031 showed no detectable components by GC/MS and was analyzed by SIM, as were all remaining filter extracts.

SIM Analysis

Results from the GC/MS analysis of 3F-017, 3F-031, and PG-2 were confirmed by SIM analysis and are given in Table 9. Results from SIM analysis of PG-2 are shown in Figure 2. Because the SIM analyses were run on sample concentrates after 4 months storage, and relative concentration factors between solvent and sample are different and unknown, only a qualitative comparison is possible.

Table 10 and Figure 3 summarize the results of the SIM analyses of the dichotomous filter extracts with the BJ solvent. The results are given in estimated concentration levels for 27 organic compounds found in extracts of 6 filters and a system blank. Identity was made by characteristic ions and retention times. The procedure used was to run a SIM system blank for the GS/MS system prior to a series of sample runs by injecting a 2 µl sample of

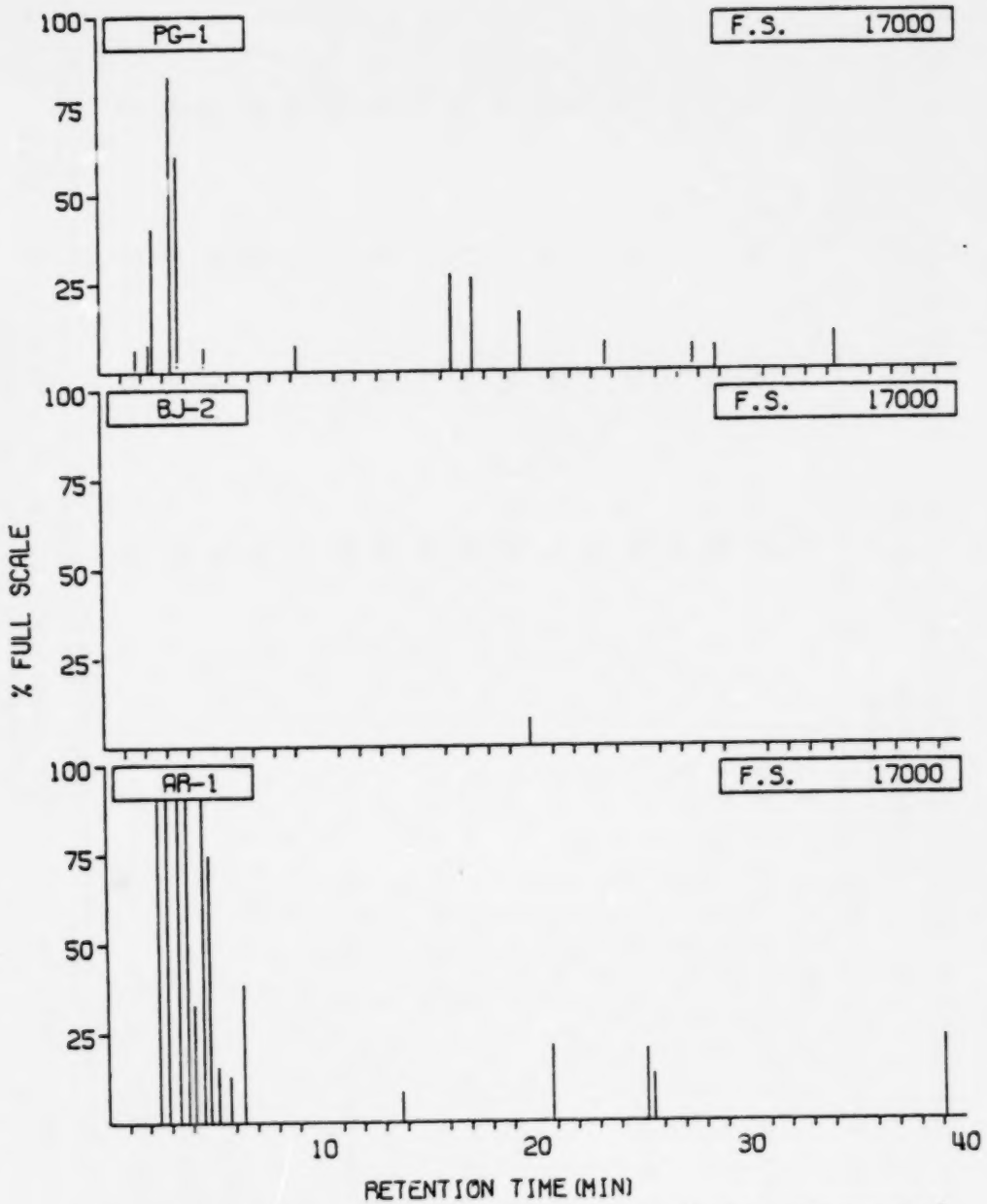


Figure 1. GCPLOT of analysis of methanol solvents concentrated as procedure blank

TABLE 9

SIM DATA* FOR DICHOTOMOUS FILTERS USING PG SOLVENT

Compound	m/e	Retention Time in minutes	System Blank	PG-2	3F-017	3F-031
Biphenyl	154.1	3.0	ND	10	1	2
Acenaphthalene	154.1	5.0	ND	ND	ND	ND
n-$C_{16}H_{34}$	85.1	5.4	ND	26	4	6
n-$C_{17}H_{36}$	85.1	7.6	ND	35	6	9
Dimethyl Phthalate	163.1	9.0	ND	ND	ND	ND
n-$C_{18}H_{38}$	85.1	9.8	ND	35	6	12
Fluorene	166.1	10.0	ND	ND	ND	ND
Methyl Myristate	74.1	10.1	ND	270	8	9
Diethyl Phthalate	149.1	10.5	ND	ND	ND	ND
Anthracene	178.1	11.0	ND	ND	2	3
n-$C_{19}H_{40}$	85.1	11.5	ND	26	6	6
Methyl Palmitate	74.1	14.0	ND	2200	150	600
n-$C_{20}H_{42}$	85.1	14.5	ND	ND	ND	ND
n-$C_{21}H_{44}$	85.1	16.5	ND	ND	ND	ND
Dibutyl Phthalate	149.1	17.0	ND	120	50	80
Methyl Oleate	74.1	17.5	ND	110	8	30
Methyl Stearate	74.1	18.0	ND	550	48	2

*Data are presented only for qualitative comparisons and are given in SIM peak heights. Concentration factors and sample age differ considerably between PG-2 and samples.

TABLE 9 (Cont.)

SIM DATA FOR DICHOTOMOUS FILTERS USING PG SOLVENT

Compound	m/e	Retention Time in minutes	System Blank	PG-2	3F-017	3F-031
n-$C_{22}H_{46}$	85.5	18.5	ND	ND	ND	ND
Fluoranthene	202.1	19.5	ND	6	5	11
n-$C_{23}H_{46}$	85.1	20.5	ND	17	ND	6
Pyrene	202.1	20.6	ND	21	3	4
n-$C_{24}H_{50}$	85.1	22.5	ND	9	ND	6
n-$C_{25}H_{52}$	85.1	24.5	ND	9	ND	6
n-$C_{26}H_{54}$	85.1	26.0	ND	ND	ND	6
Dioctyl Phthalate	149.1	28.0	12	170	140	370
Benzo[k]fluor-anthene	252.1	35.0	ND	ND	0.5	0.1
Benzo[a]pyrene	252.1	37.0	.3	ND	2	5

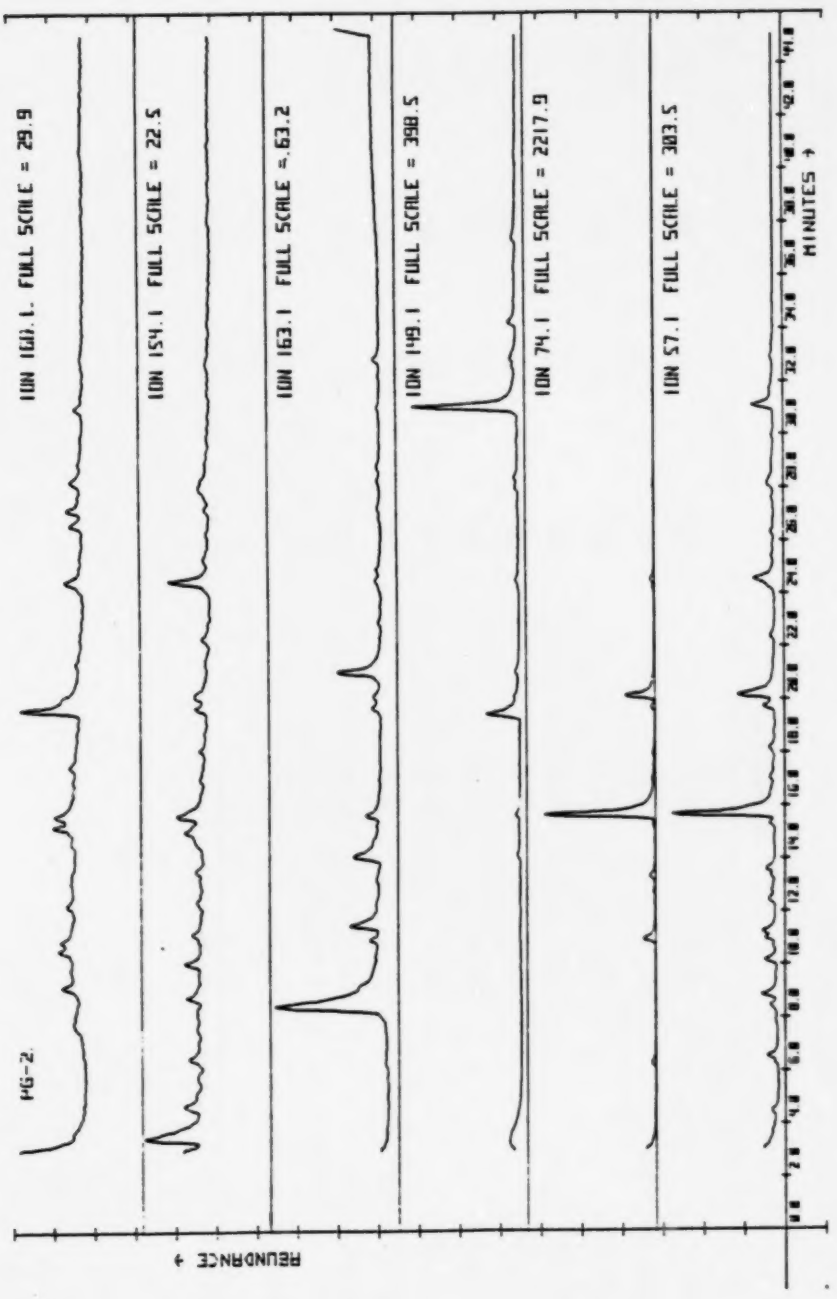

PG-2
ION 160.1 FULL SCALE = 29.9
ION 154.1 FULL SCALE = 22.5
ION 163.1 FULL SCALE = 63.2
ION 149.1 FULL SCALE = 398.5
ION 74.1 FULL SCALE = 2217.9
ION 57.1 FULL SCALE = 303.5
ABUNDANCE
MINUTES

Figure 2. SIM plot of PG-2 analysis

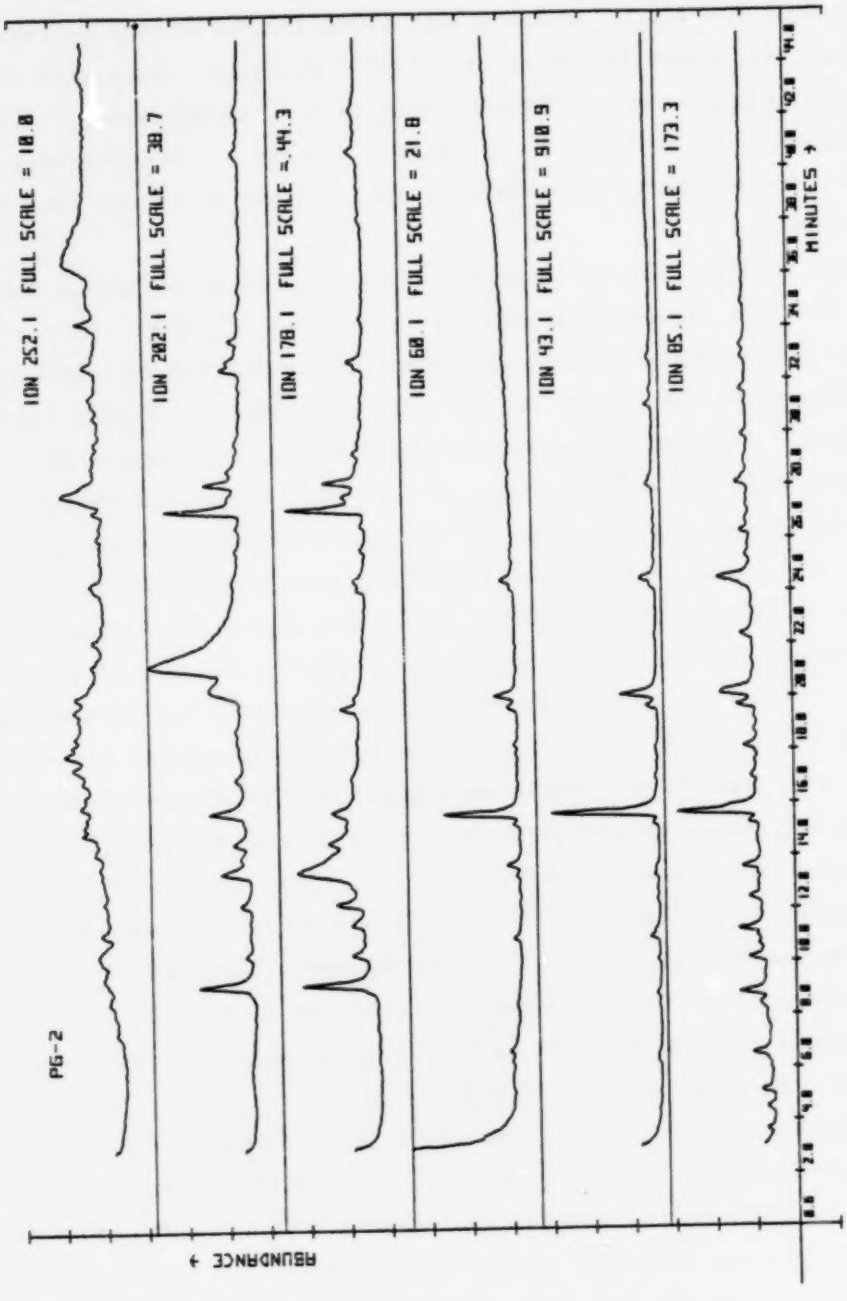

PG-2
ION 252.1 FULL SCALE = 10.0
ION 202.1 FULL SCALE = 38.7
ION 178.1 FULL SCALE = 44.3
ION 68.1 FULL SCALE = 21.8
ION 43.1 FULL SCALE = 918.9
ION 85.1 FULL SCALE = 173.3
ABUNDANCE
MINUTES

Figure 2. (Cont.) SIM plot of PG-2 analysis

pure BJ methanol. This gives the background SIM components contributed by the syringe needle, septum puncture, GC column and other unknown elements. The system blanks run prior to each series of analyses were almost identical to the typical one listed in Table 10. Using the difference between these values and those found in the filter extract analyses, along with the SIM peak values from a known calibration mixture run, an estimate of quantities of components given in Table 10 was made. Figures 4,5,6 containing the data for sample 3F-016 illustrate this procedure. Other pertinent data are given in the appendix.

Table 10 shows that most organic compounds detected are at low concentrations and that instrumental artifacts are also very low. Filter blanks 3C-033 and 3F-033 appear to contain methyl myristate, methyl palmitate, and methyl stearate at net higher levels than after similar filters had been used for sampling. Although no unequivocal explanation is possible for these data, they suggest that the large volumes of air passing over the filters during sampling may remove esters which are present as initial impurities. Each filter contains a range of n-hydrocarbons which are detected at quantities above that found on the fine filter blank. Only n-$C_{21}H_{44}$ and n-$C_{22}H_{46}$ were significantly larger on the blanks than on the filters. Filters 3F-028 and 3F-032 had increased levels of dibutyl phthalate, while other filters had levels at or near those of the filter blank. No dimethyl phthalate or diethyl phthalate were seen in any sample or blank. Levels of dioctyl phthalate were 10 to 20 ng/m^3, but similar levels were also present in the filter blanks. Significantly, four common aromatic and polynuclear aromatic hydrocarbons were not detected in filter blanks or filter samples. These compounds were biphenyl, acenaphthene, fluorene, and anthracene. A trace of fluoranthene might have been in 3F-033 and pyrene was detected in 3F-016, 3F-028, and 3C-031. Benzo[a]pyrene and benzo[k]fluoranthene were also detected at levels from 0.1 to 1 ng/m^3 in 3F-016, 3F-028, and 3C-031.

In summary, a few of the dichotomous filters analyzed in this study contained very low levels of some other common polynuclear aromatic hydrocarb s. Low levels of n-alkanes were detected in every filter sample and a new loss in methyl esters was observed between filter blanks and filter samples. The quantities found, in the 0.1 to 10 ng/m^3 range, were at the detection limits of the procedure used. This indicates very low loading of organic compounds

TABLE 10

CONCENTRATIONS (ng/m^3)* OF ORGANIC COMPOUNDS
IN DICHOTOMOUS FILTER EXTRACTS

Compound	m/e	Retention Times in minutes	System Blank	3C-033 Filter Blank	3F-033 Filter Blank	3F-016	3F-028	3F-032	3C-031
Biphenyl	154.1	3.0	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	154.1	5.0	ND	ND	ND	ND	ND	ND	ND
n-$C_{16}H_{34}$	85.1	5.4	ND	ND	ND	<0.1	ND	ND	<0.1
n-$C_{17}H_{36}$	85.1	7.6	ND	ND	ND	<0.1	ND	ND	<0.1
Dimethyl Phthalate	163.1	9.0	ND	ND	ND	ND	ND	ND	ND
n-$C_{18}H_{38}$	85.1	9.8	ND	ND	ND	<0.1	ND	ND	0.1
Fluorene	166.1	10.0	ND	ND	ND	ND	ND	ND	ND
Methyl Myristate	74.1	10.1	ND	0.6	0.5	<0.1	ND	<0.1	0.3
Diethyl Phthalate	149.1	10.5	ND	ND	ND	ND	ND	ND	ND
Anthracene	178.1	11.0	ND	ND	ND	ND	ND	ND	ND
n-$C_{19}H_{40}$	85.1	11.5	ND	ND	ND	<0.1	<0.1	ND	0.1
Methyl Palmitate	74.1	14.0	ND	4	5	0.3	0.8	0.6	5
n-$C_{20}H_{92}$	85.1	14.5	ND	<0.1	ND	<0.1	<0.1	0.6	0.3

ND is not detected. <0.1 indicates a range of 0.01 to 0.09

*estimated precision = ±50%

TABLE 10 (Cont.)

CONCENTRATIONS (ng/m^3)* OF ORGANIC COMPOUNDS
IN DICHOTOMOUS FILTER EXTRACTS

Compound	m/e	Retention Times in Minutes	System Blank	3C-033 Filter Blank	3F-033 Filter Blank	3F-016	3F-028	3F-032	3C-031
n-$C_{21}H_{44}$	85.1	16.5	ND	2	0.5	<0.1	0.2	2	0.4
Dibutyl (1) phthalate	149.1	17	ND	2	1	1	4	150	2
Methyl oleate	74.1	17.5	ND	0.4	ND	ND	ND	0.2	0.4
Methyl stearate	74.1	18	ND	2	2	0.3	0.5	0.8	2
n-$C_{22}H_{46}$	85.1	18.5	ND	0.2	<0.1	<0.1	<0.1	3	<0.1
Fluoranthene	202.1	19.5	ND	ND	<0.1	ND	ND	ND	ND
n-$C_{33}H_{48}$	85.1	20.5	ND	ND	ND	<0.1	<0.1	1.6	<0.1
Pyrene	202.1	20.6	0.2	0.4	ND	1	0.4	ND	1
n-$C_{24}H_{50}$	85.1	22.5	ND	ND	ND	<0.1	<0.1	1	0.1
n-$C_{25}H_{52}$	85.1	24.5	ND	ND	ND	<0.1	<0.1	1	<0.1
n-$C_{26}H_{54}$	85.1	26.0	ND	ND	ND	<0.1	<0.1	0.5	<0.1
Dioctyl phthalate	179.1	28.0	10	20	10	10	20	20	20
Benzo[k] Fluoranthene*	252.1	35	ND	ND	ND	0.2	0.1	ND	<0.1
Benzo[a]pyrene	252.1	37	0.3	<0.1	ND	1	0.1	ND	1

(1) Based on relative response factor for B[a] of 0.6. * Based on B[a]p = 0.7

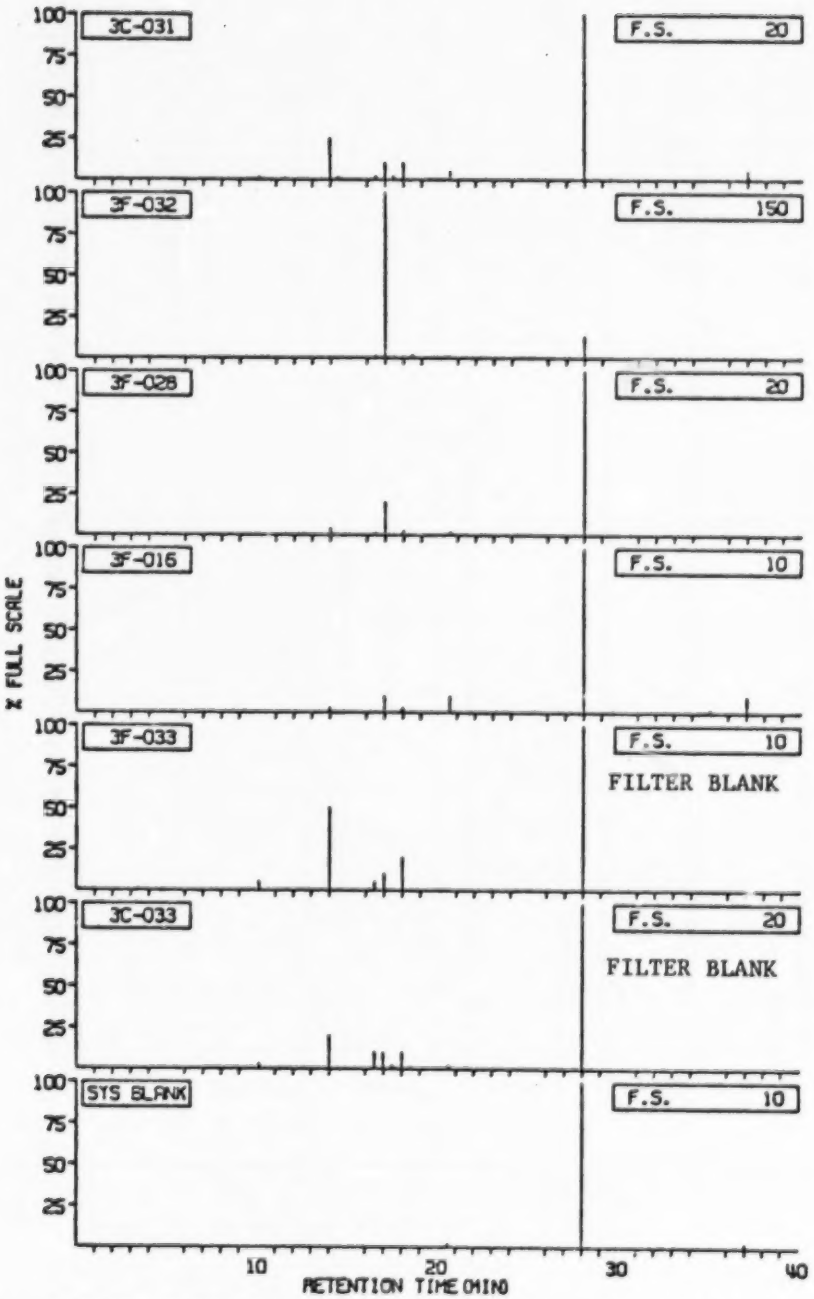


Figure 3. GCPLOT of SIM data for dichotomous filters in full scale (F.S.) of ng/m^3

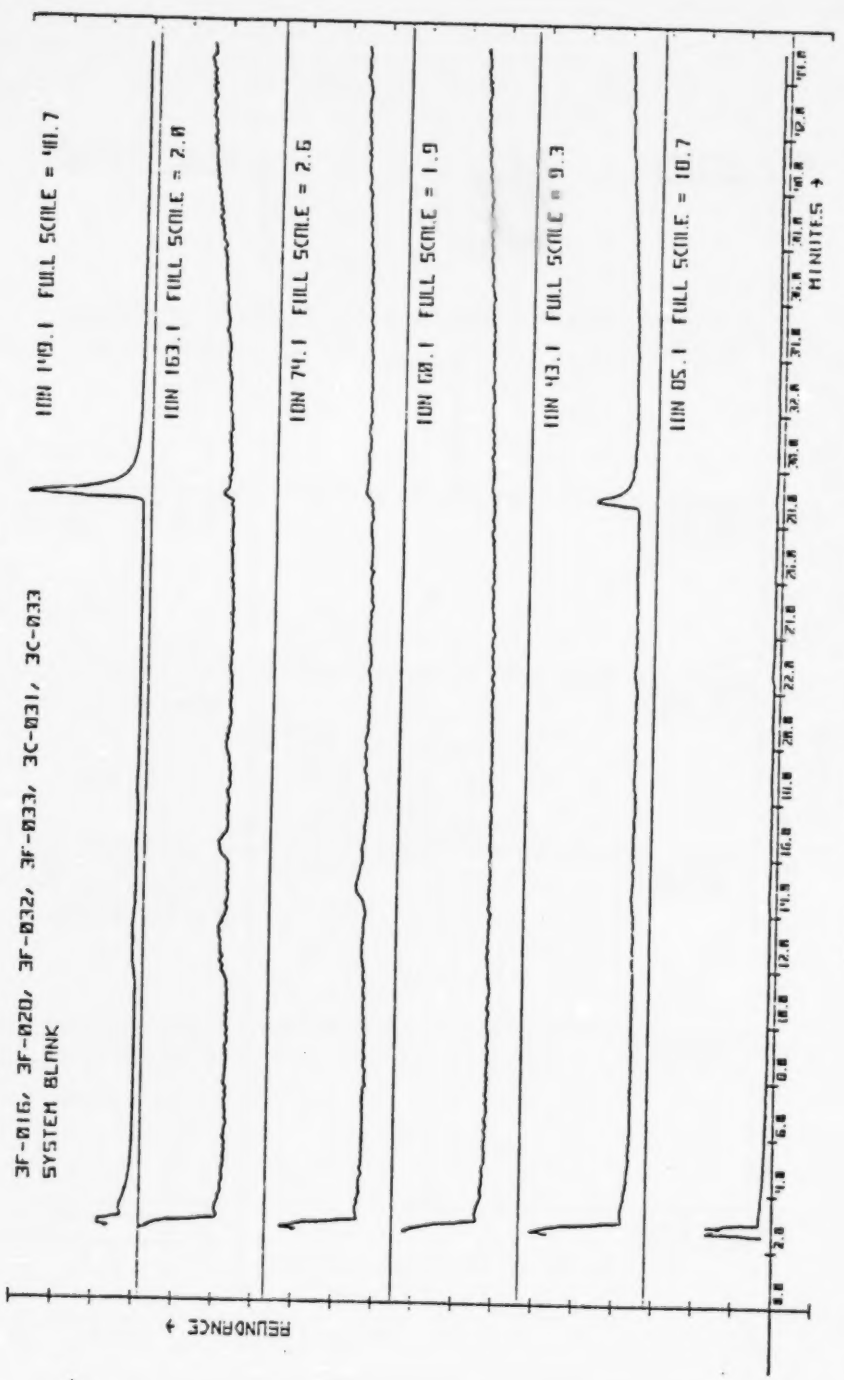

3F-016, 3F-020, 3F-032, 3F-033, 3C-031, 3C-033
SYSTEM BLANK
ION 149.1 FULL SCALE = 481.7
ION 163.1 FULL SCALE = 2.8
ION 74.1 FULL SCALE = 2.6
ION 68.1 FULL SCALE = 1.9
ION 43.1 FULL SCALE = 9.3
ION 85.1 FULL SCALE = 10.7
ABUNDANCE
MINUTES

Figure 4. SIM plot of system blank for 3F-016

Reproduced from best available copy.

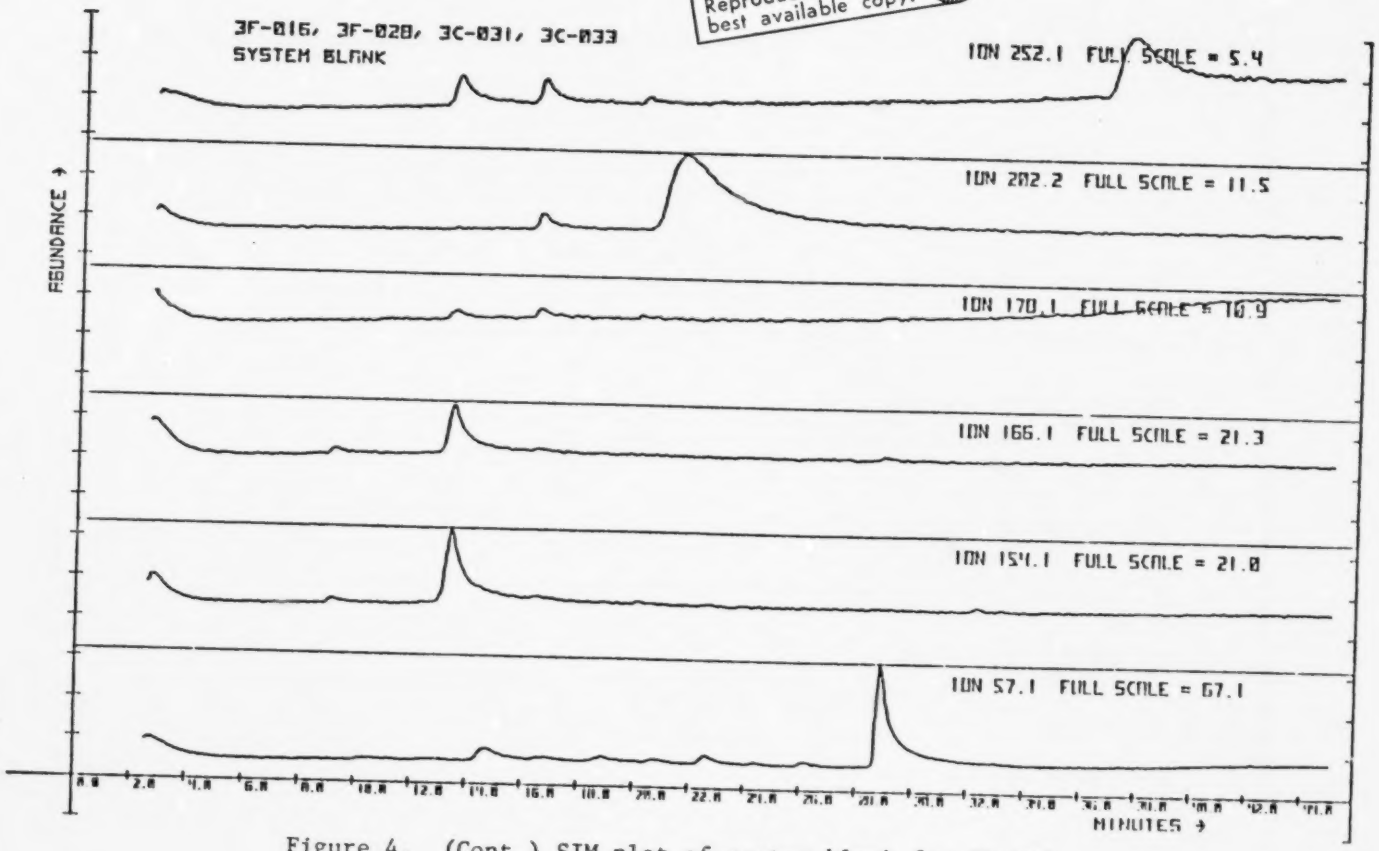

3F-016, 3F-028, 3C-031, 3C-033
SYSTEM BLANK
ION 252.1 FULL SCALE = 5.4
ION 202.2 FULL SCALE = 11.5
ION 170.1 FULL SCALE = 10.9
ION 166.1 FULL SCALE = 21.3
ION 154.1 FULL SCALE = 21.0
ION 57.1 FULL SCALE = 67.1
ABUNDANCE →
MINUTES →

Figure 4. (Cont.) SIM plot of system blank for 3F-016

Reproduced from
best available copy.

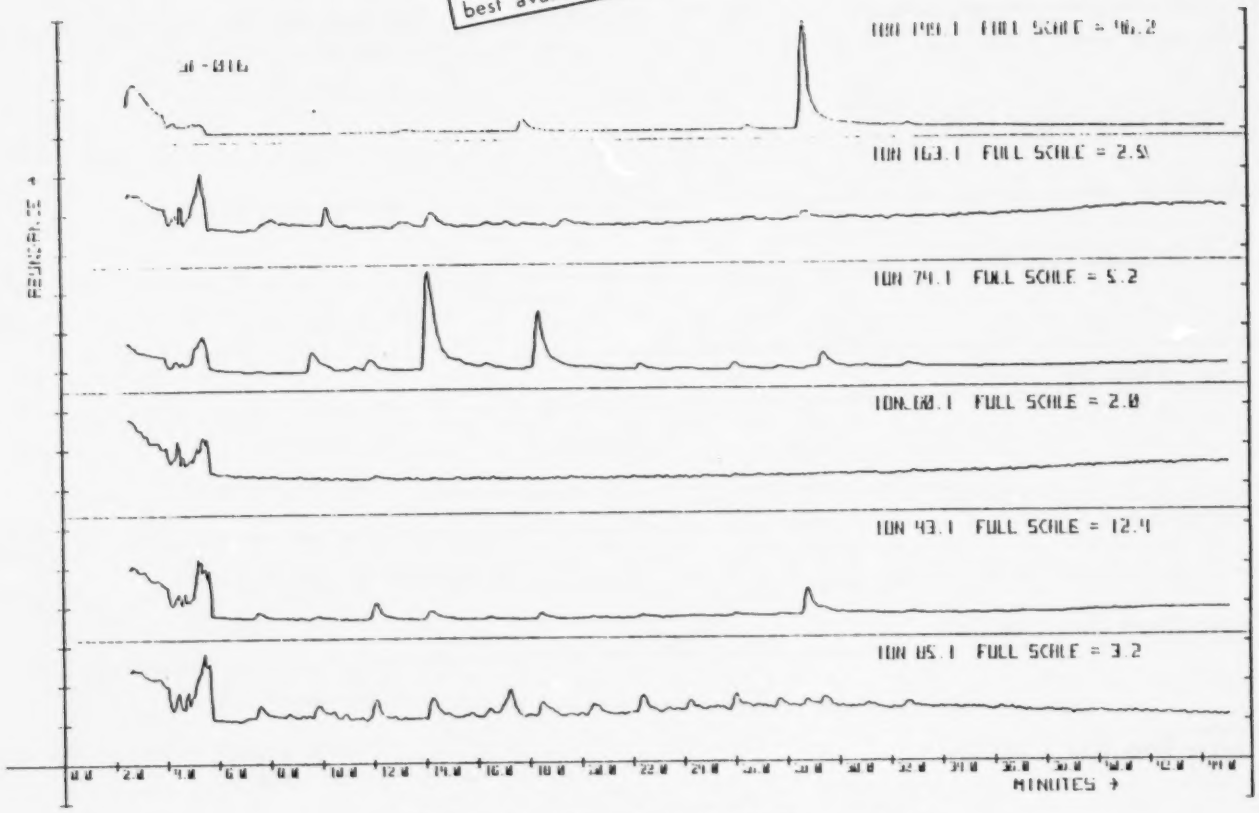


Figure 5. SIM plot of 3F-016 analysis

Reproduced from
best available copy.

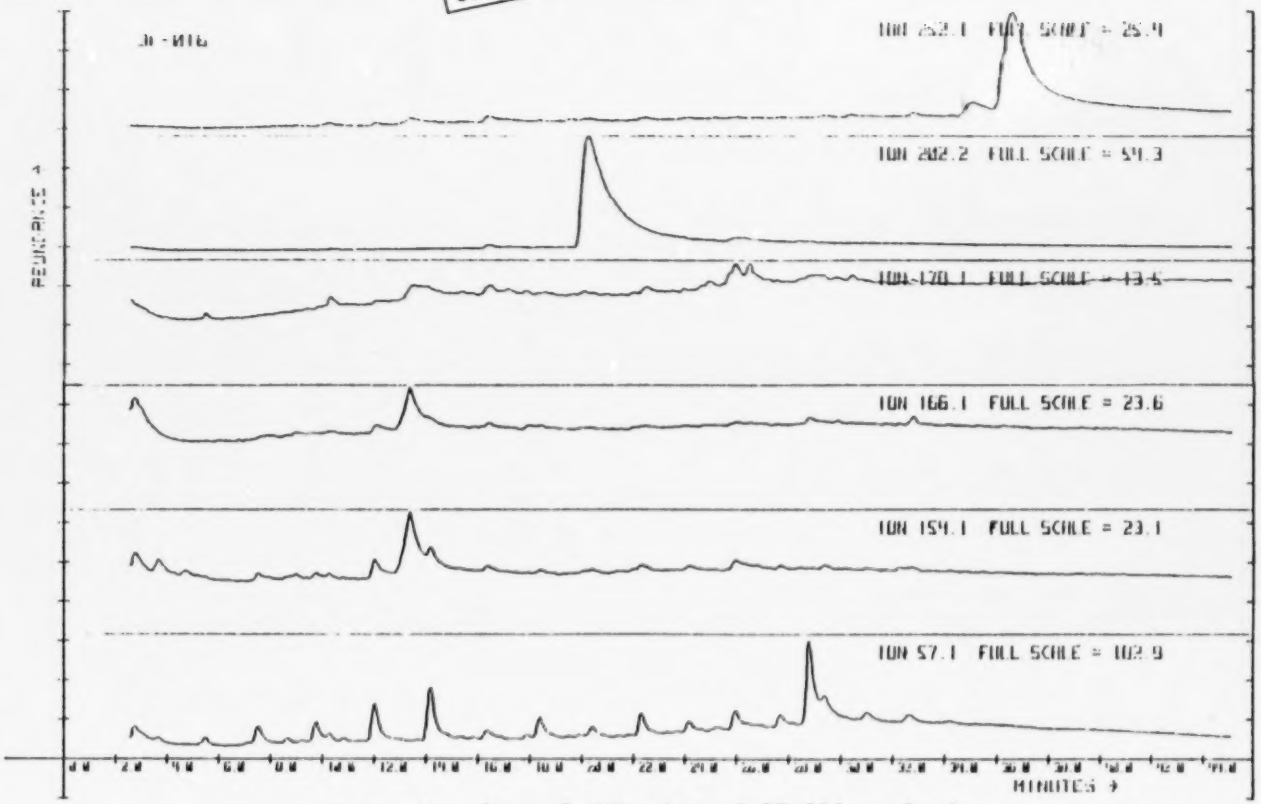

3F-016
ION 282.1 FULL SCALE = 25.4
ION 282.2 FULL SCALE = 54.3
ION 170.1 FULL SCALE = 13.5
ION 166.1 FULL SCALE = 23.6
ION 154.1 FULL SCALE = 23.1
ION 57.1 FULL SCALE = 102.9
MINUTES →

Figure 5. (Cont.) SIM plot of 3F-016 analysis

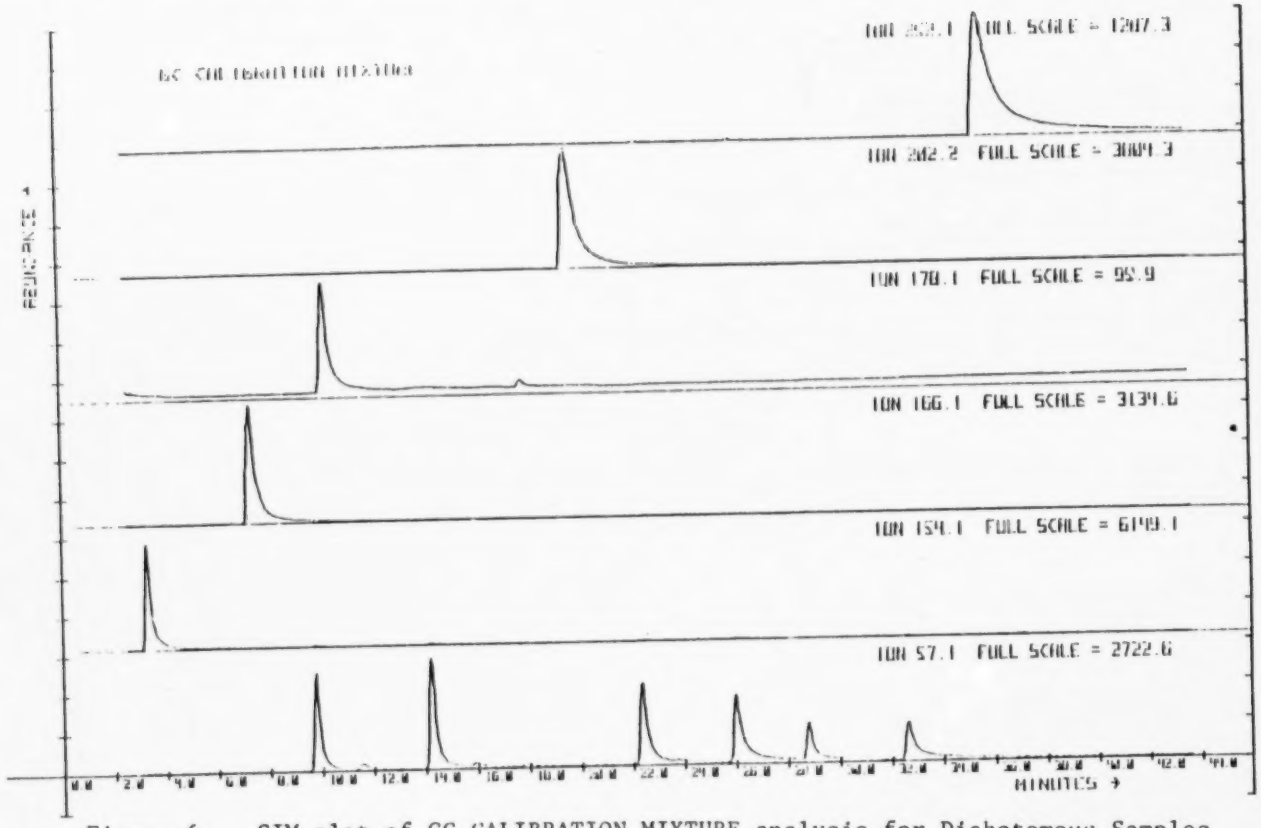

ABUNDANCE
ION 262.2 FULL SCALE = 3884.3
ION 178.1 FULL SCALE = 95.9
ION 166.1 FULL SCALE = 3134.6
ION 154.1 FULL SCALE = 6198.1
ION 57.1 FULL SCALE = 2722.6
MINUTES →

Figure 6. SIM plot of GC CALIBRATION MIXTURE analysis for Dichotomous Samples

on the dichotomous filters. A direct comparison of the organic loading extracted from these filter samples with those from lightly loaded Hi-Vol filters can be seen by comparing the GCPLOTS of these two sample sets shown in Figures 7 & 8. In general, the intensity of the GC peaks for the Hi-Vol samples were greater by a factor of 10. The Hi-Vol blank filter element also showed less organic compounds, indicating it was cleaned more rigorously than were the dichotomous filter elements.

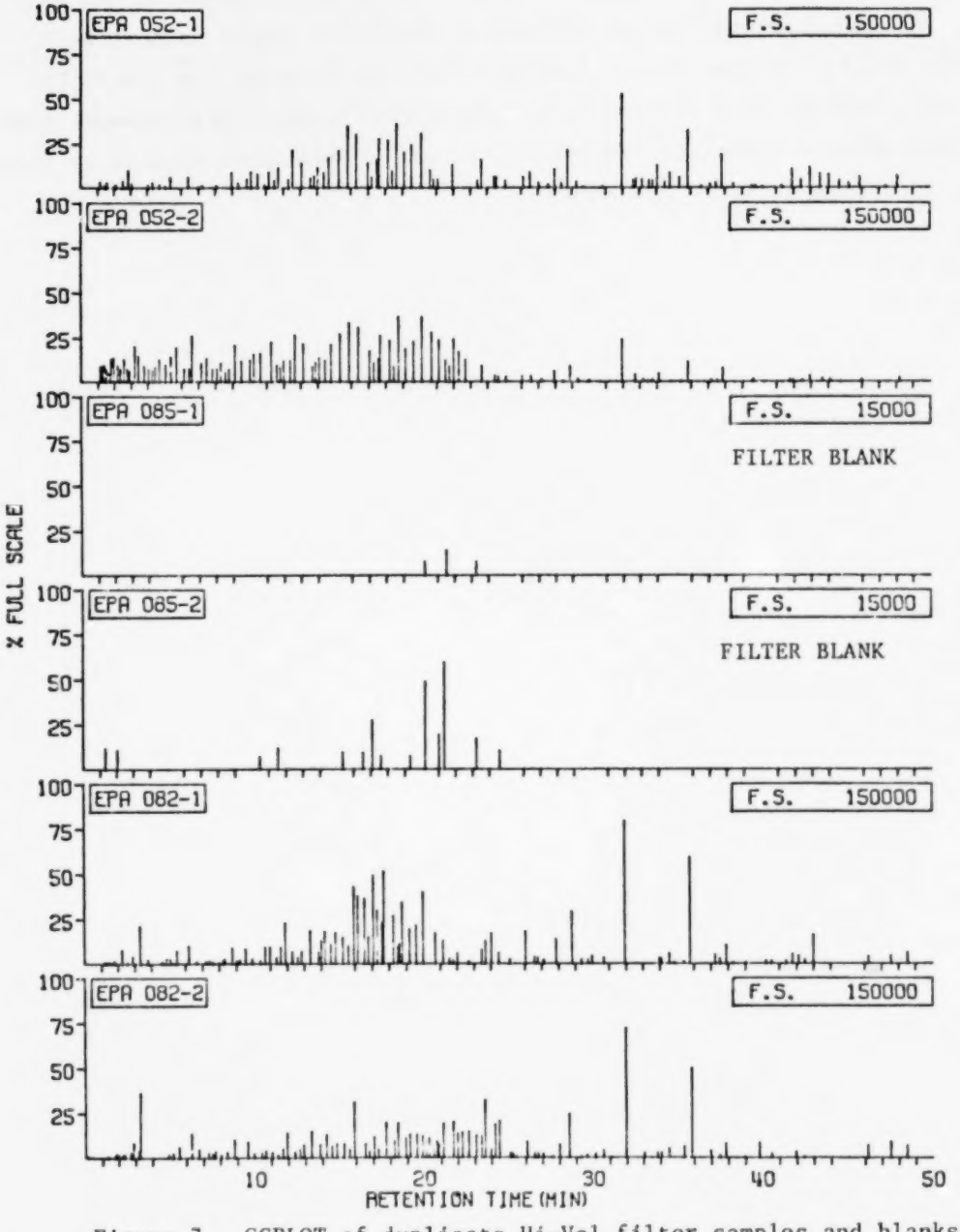


Figure 7. GCPLOT of duplicate Hi-Vol filter samples and blanks

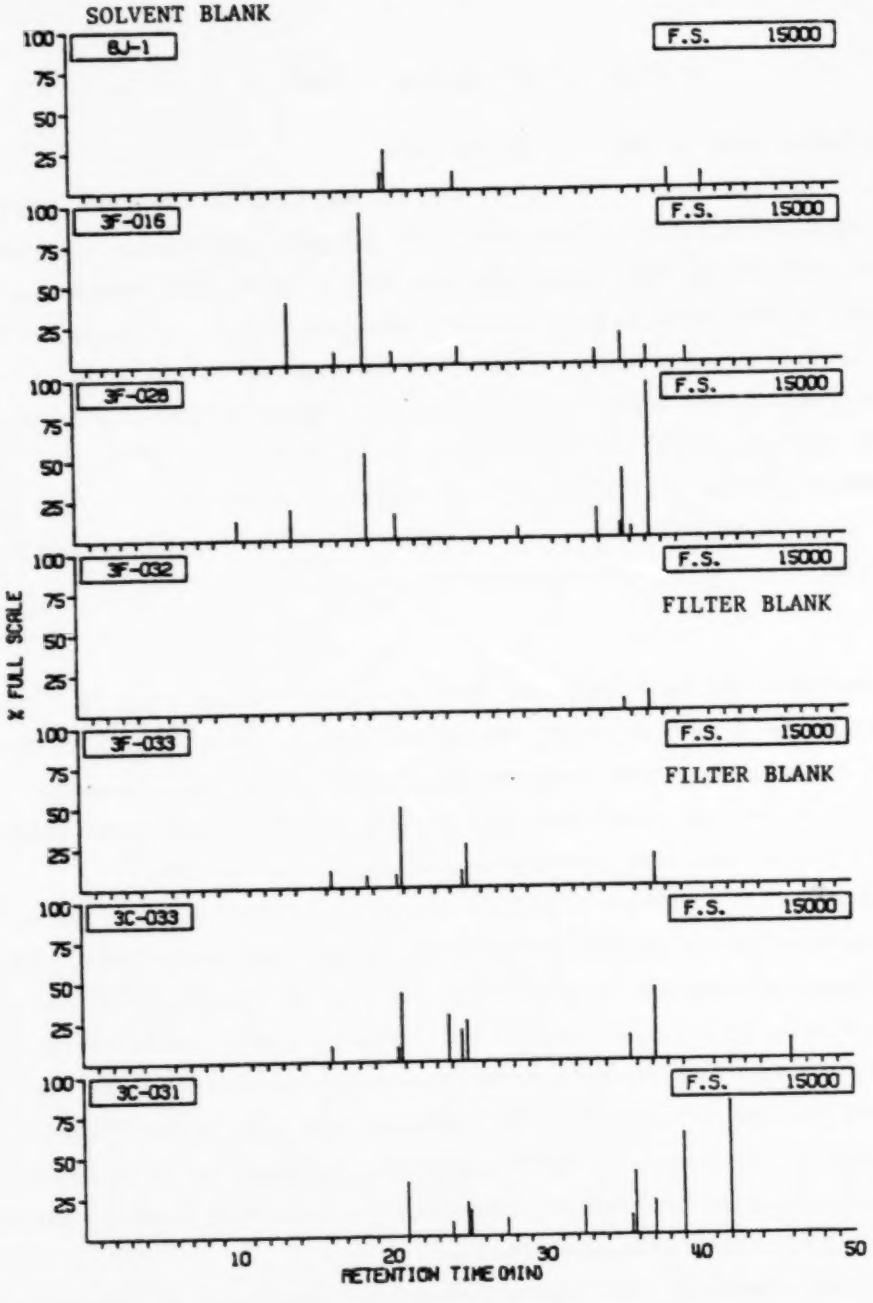


Figure 8. GCPLOT of dichotomous filter samples and solvent blank

RESULTS AND DISCUSSION - PART II

GC/MS ANALYSIS - HIGH VOLUME FILTER ANALYSIS

Visual inspection of the two Hi-Vol filter samples analyzed, 0052 and 0086, indicated that both filters contained a light particulate loading. One-half of each filter was chosen for analysis. Each half chosen was further divided so that four filter portions were available for separate extraction and analysis, each portion comprising one-quarter of the original filter. The two quarter-filters from filter 0052 are designated 0052-1 and 0052-2, and the two quarter-filters from 0086 are called 0086-1 and 0086-2. This analysis scheme allows evaluation of the reproducibility of the procedures employed. Regular GC/MS analysis was difficult due to the light particulate loadings, therefore GC/MS SIM analysis was employed.

GC/MS SIM

SIM analysis for both 0052 and 0086 produced similar results. Comparisons between plots of SIM data for duplicate samples (0052-1 with 0052-2 and 0086-1 with 0086-2) show good reproducibility of the analytical method (Figures 9-12). Retention times and peak shapes for major and minor components in duplicate filter extracts are almost identical qualitatively.

A comparison of full-scale values between Figures 11 and 12 shows quantitative reproducibility within a factor of two for most compounds. This holds for components present at levels approaching the sensitivity limits for GC/MS-SIM analysis. The good reproducibility also demonstrates the even distribution of organic compounds on corresponding quarter-filters sections. Sample 0052-2 reached dryness after GC analysis and was reconstituted with 50 microliters of methanol before GC/MS analysis. No qualitative changes are apparent, however some quantitative changes were detected, most notably a decrease in methyl ester concentration.

Data shown previously in Figure 7 compares results of GC analysis of duplicate sample sets from filters 0052, 0086 and a Hi-Vol filter blank

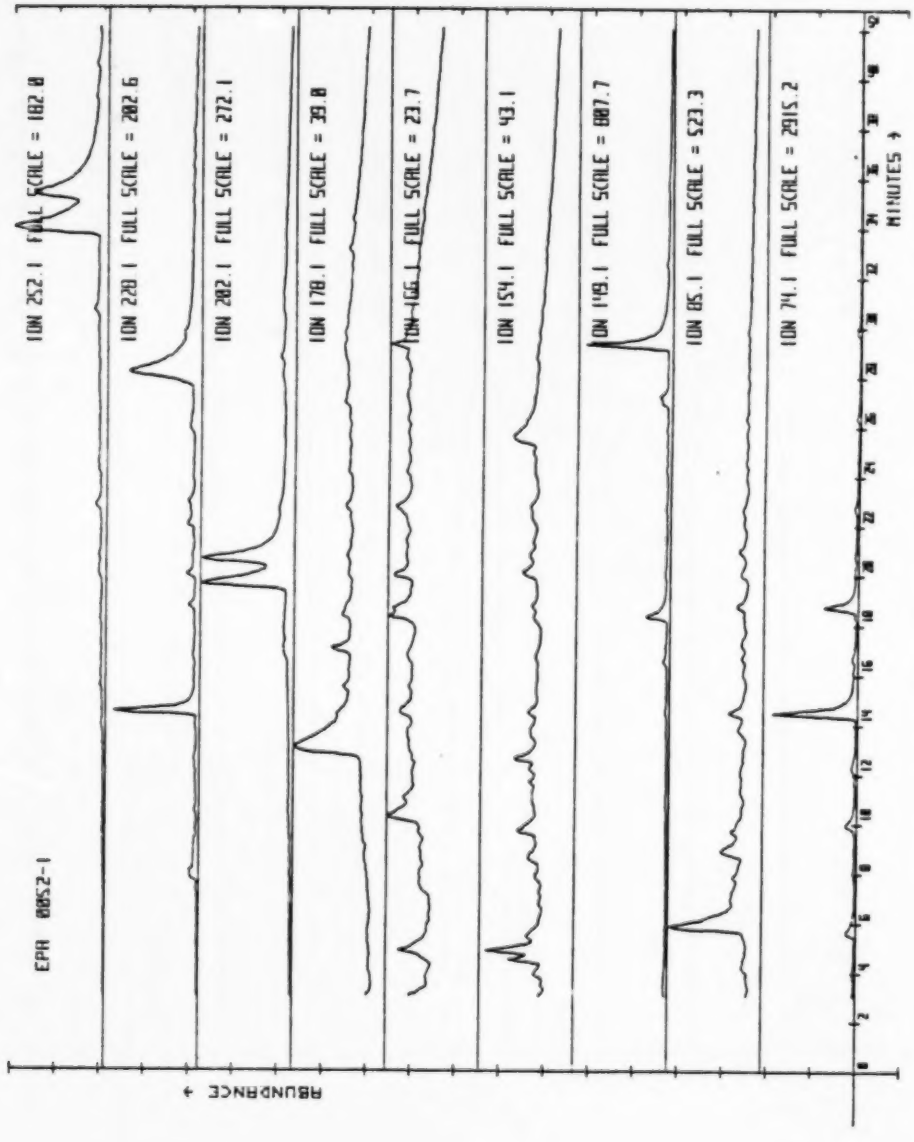

EPA 0052-1
ION 252.1 FULL SCALE = 182.0
ION 220.1 FULL SCALE = 202.6
ION 202.1 FULL SCALE = 272.1
ION 178.1 FULL SCALE = 39.8
ION 166.1 FULL SCALE = 23.7
ION 154.1 FULL SCALE = 43.1
ION 149.1 FULL SCALE = 887.7
ION 85.1 FULL SCALE = 523.3
ION 74.1 FULL SCALE = 2915.2
ABUNDANCE →
MINUTES →

Figure 9. SIM plot of Hi-Vol sample 0052-1

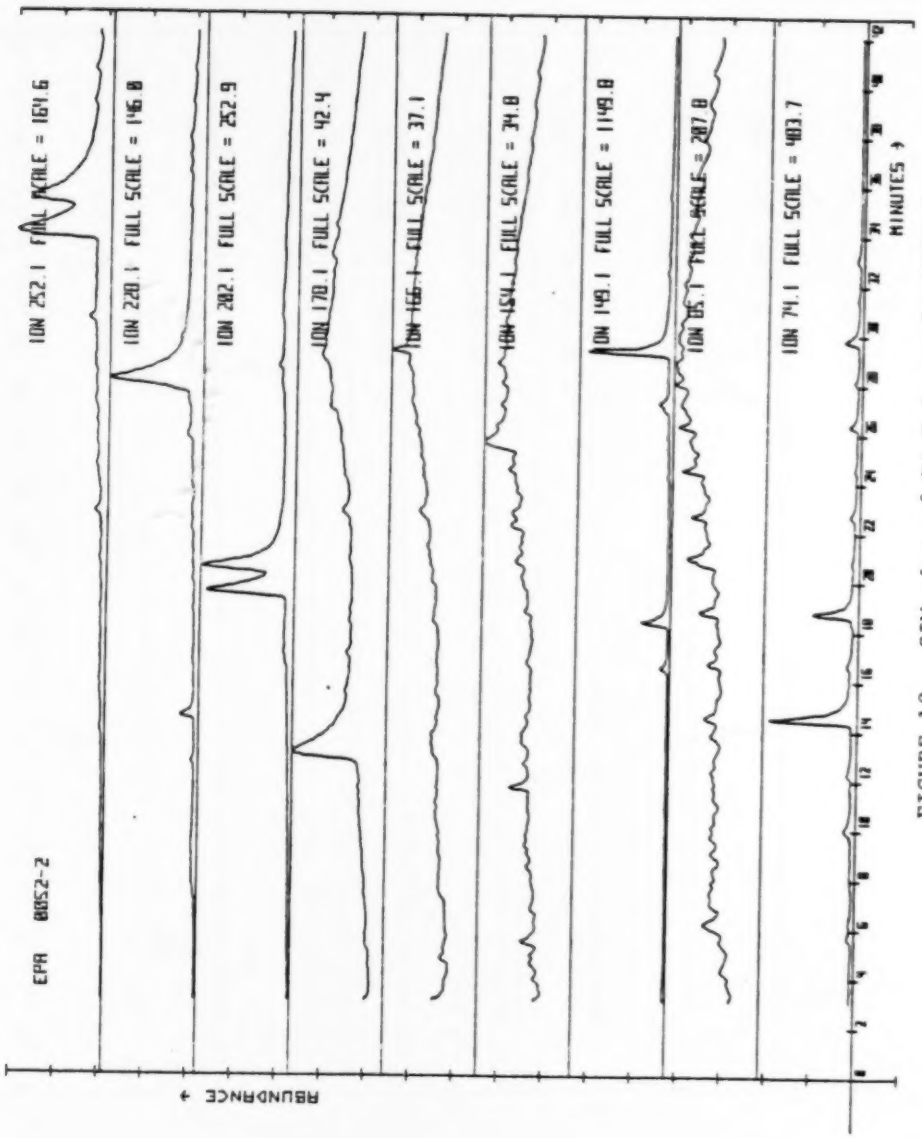

EPA 0052-2
ION 252.1 FULL SCALE = 164.6
ION 220.1 FULL SCALE = 146.8
ION 202.1 FULL SCALE = 252.9
ION 178.1 FULL SCALE = 42.4
ION 166.1 FULL SCALE = 37.1
ION 154.1 FULL SCALE = 34.8
ION 149.1 FULL SCALE = 1149.8
ION 85.1 FULL SCALE = 287.8
ION 74.1 FULL SCALE = 483.7
ABUNDANCE
MINUTES

FIGURE 10. SIM plot of Hi-Vol sample 0052-2

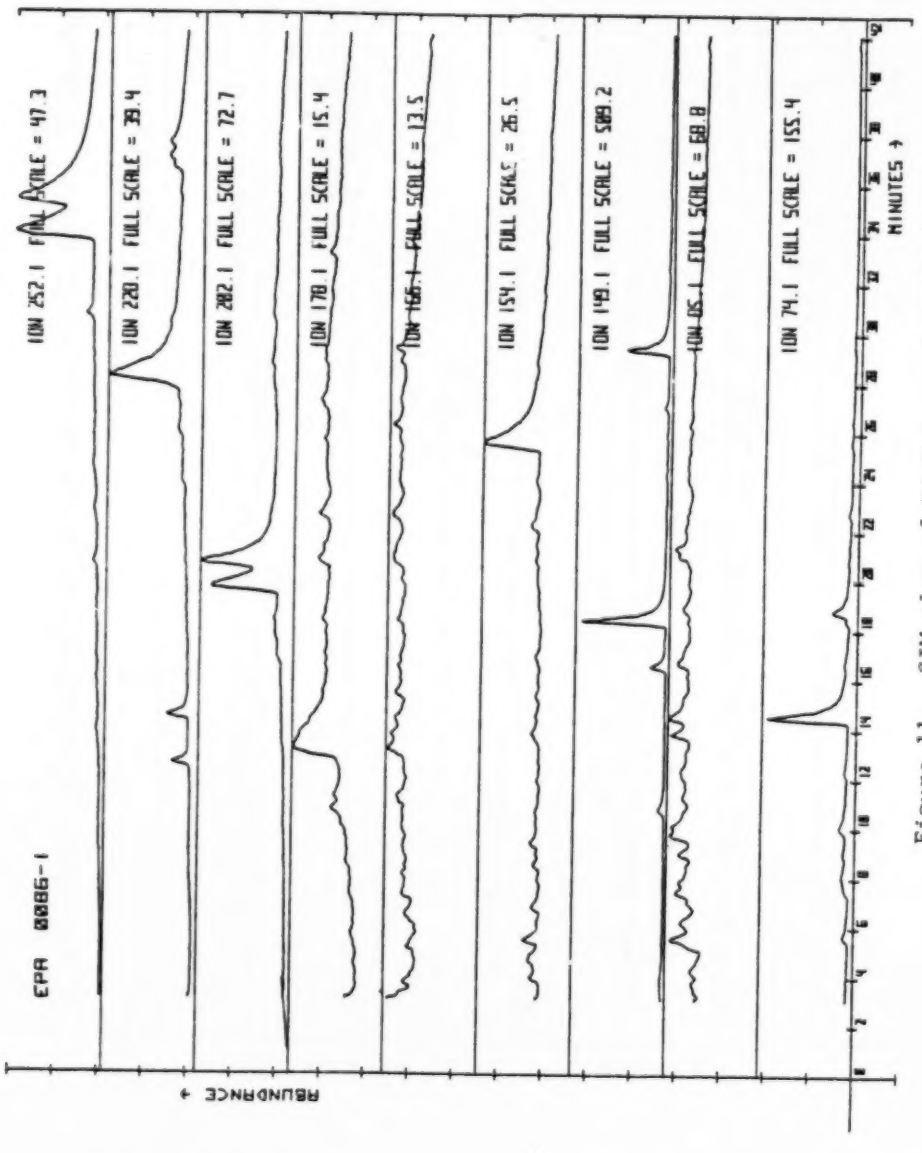

EPA 0086-1
ION 252.1 FULL SCALE = 47.3
ION 220.1 FULL SCALE = 39.4
ION 202.1 FULL SCALE = 72.7
ION 178.1 FULL SCALE = 15.4
ION 154.1 FULL SCALE = 26.5
ION 149.1 FULL SCALE = 589.2
ION 74.1 FULL SCALE = 155.4
ABUNDANCE
MINUTES

Figure 11. SIM plot of Hi-Vol sample 0086-1

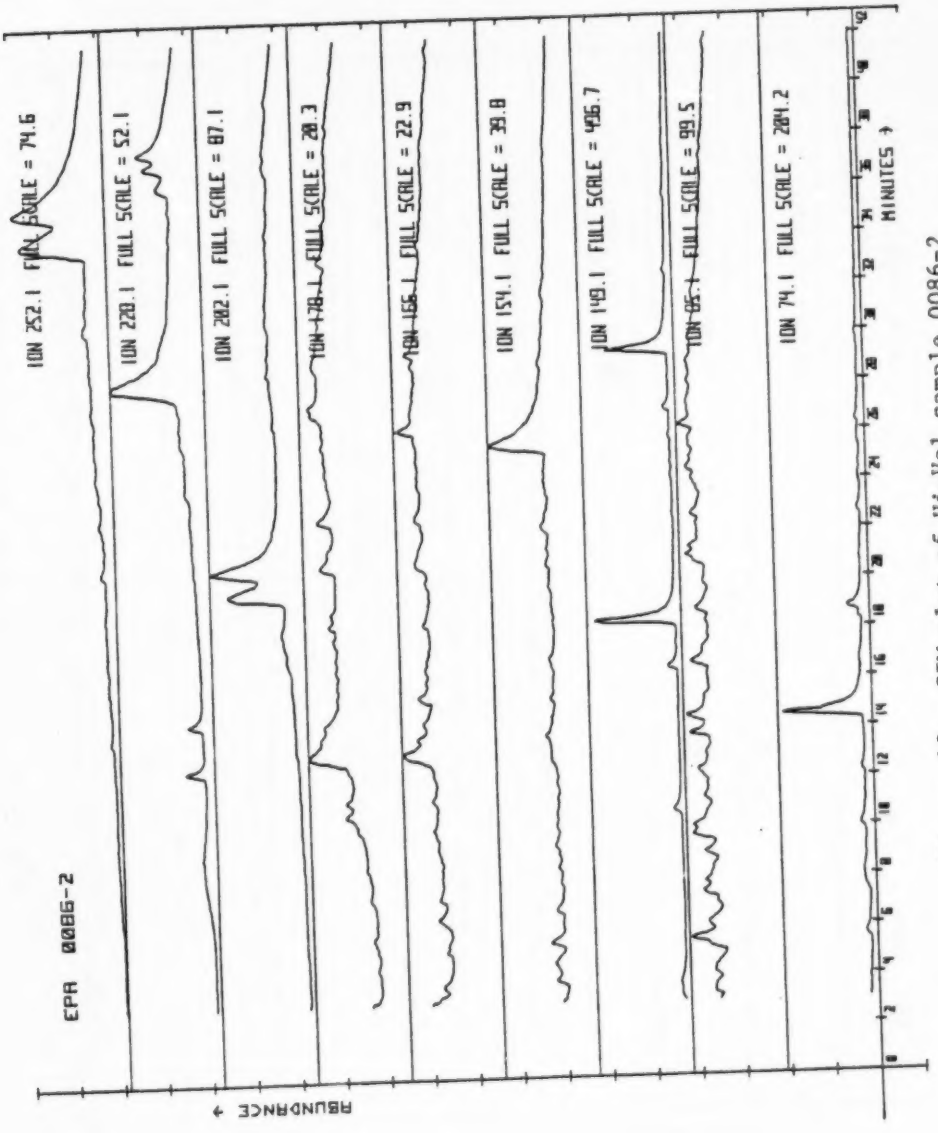

EPA 0086-2
ION 252.1 FULL SCALE = 74.6
ION 220.1 FULL SCALE = 52.1
ION 202.1 FULL SCALE = 87.1
ION 178.1 FULL SCALE = 20.3
ION 166.1 FULL SCALE = 22.9
ION 154.1 FULL SCALE = 39.8
ION 143.1 FULL SCALE = 406.7
ION 85.1 FULL SCALE = 99.5
ION 74.1 FULL SCALE = 2841.2
ABUNDANCE
MINUTES

Figure 12. SIM plot of Hi-Vol sample 0086-2

(sample 0085). Plots are at full scale sensitivity values which are comparable to relative condensation factors. The filter blank shows very low levels of only a few contaminants. These data further support the qualitative and quantitative reproducibility of the analytical procedure.

Table 11 and Figure 13 show the SIM data from analysis of 0052-1 and 0082-1. Quantitation is based on comparison of sample component peak heights to peak heights of standards. Calculations include corrections for injection volumes, sample volume changes, volume of air sampled and relative response factors. Independent quantitation by GC-FID confirmed the estimated concentration range for most compounds detected to be from 1 to 17 ng/m^3. Most compounds detected were found in all the filter extracts and at similar concentrations. Only dioctyl phthalate, methyl palmitate and methyl stearate were found to differ significantly between the samples. Some methyl esters, other phthalates and n-hydrocarbons were not detected in the SIM analysis.

GC/MS Analysis - Generation of Mass Chromatograms

Software [Dual-Mode] has been developed at the University of Waterloo which allows storage of the total ion current and up to 6 mass chromatograms in a GC/MS run, in addition to the mass spectra taken at the top of eluting GC peaks (16). Results of the analysis of 0052-1 and 0086-1 using the Dual-Mode program, are shown in Figures 15 and 16. These results further confirm the major differences between these two samples to be in the amounts of methyl palmitate and methyl stearate. Mass spectra contained significant contributions from unresolved and unidentified organic compounds, even after subtraction of background spectra. Much of this mass of compounds may consist of unsaturated and branched hydrocarbons. Components of low abundance detected on a high background of unresolved hydrocarbons are not easily identified. The low abundances obtained by running column blanks confirmed the presence of high background material in the samples. Mass chromatograms which were generated support results obtained from the SIM analyses.

TABLE 11

SIM QUANTITATION OF HI-VOL
SAMPLES 0052-1 and 0086-1

Compound	Retention Time in minutes	0052-1 ng/m^3	0086-1
PAHs			
Benzo[a]pyrene	35	2	1
Benzo[k]fluoranthene(1)	34	3	1
Benzanthracene (1)	28	3	1
Pyrene (2)	20.5	0.6	0.3
Fluoranthene	19.5	0.6	0.3
Anthracene	10.5		
Fluorene	7.5		
Biphenyl	3.5		
PHTHALATES			
Dioctyl Phthalate	29.3	17	11
Dibutyl Phthalate	18.3	0.6	4
Diethyl Phthalate	10.5		0.3
HYDROCARBONS	*		
Methyl Palmitate (3)	14.5	15	1
Methyl Stearate (3)	18.5	8	<0.1

(1) Based on Benzo[a]pyrene. Response Factor = 1
(2) Based on Fluoranthene. Response Factor = 1
* Retention Times are n-$C_{18}H_{40}$:10.2 minutes:n-$C_{20}H_{42}$:14.5 minutes
(3) Based on response of n-$C_{21}H_{42}$ relative response factors are 15. for Methyl Palmitate and 1.2 for Methyl Stearate.

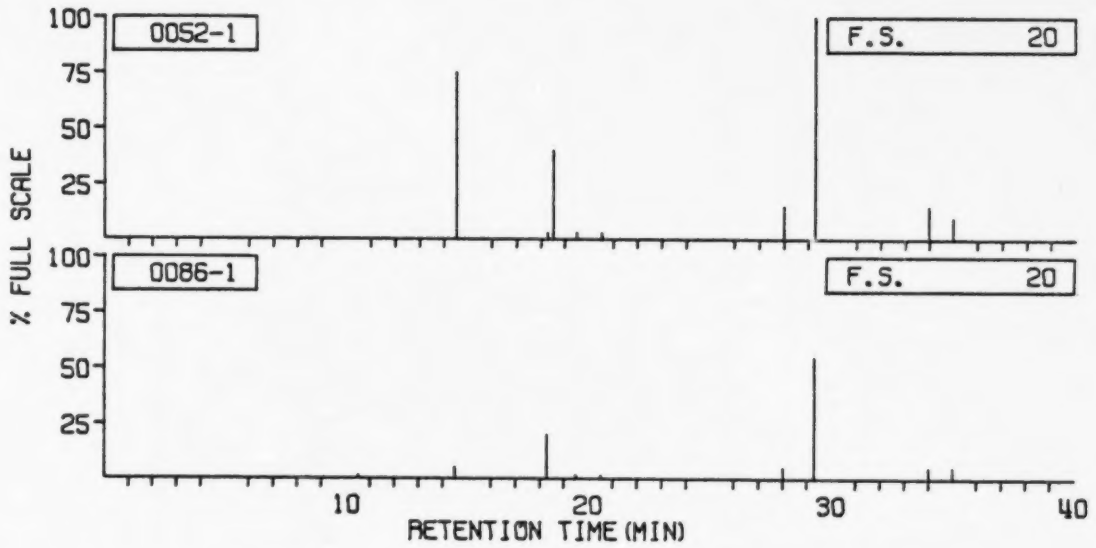


Figure 13. GCPLOT of SIM data of Hi-Vol samples 0052-1 and 0086-1 for components identified in Table 11

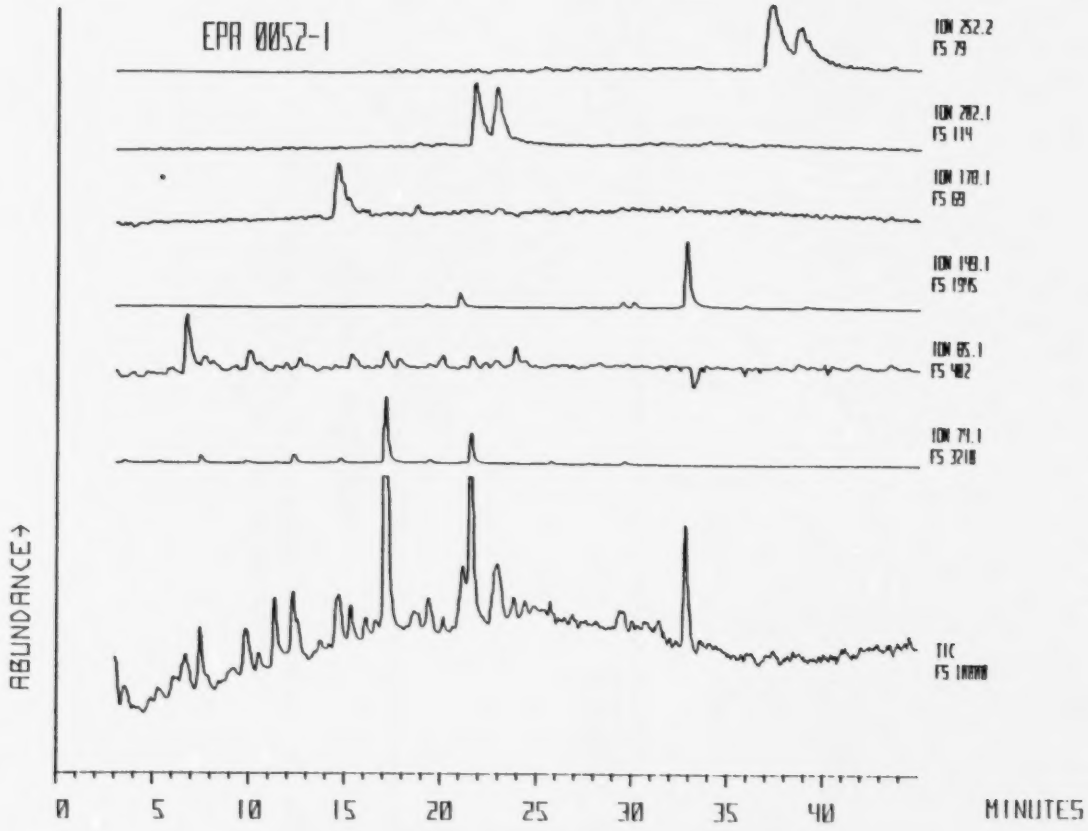


Figure 14. Plots from Dual-Mode analysis of 0052-1

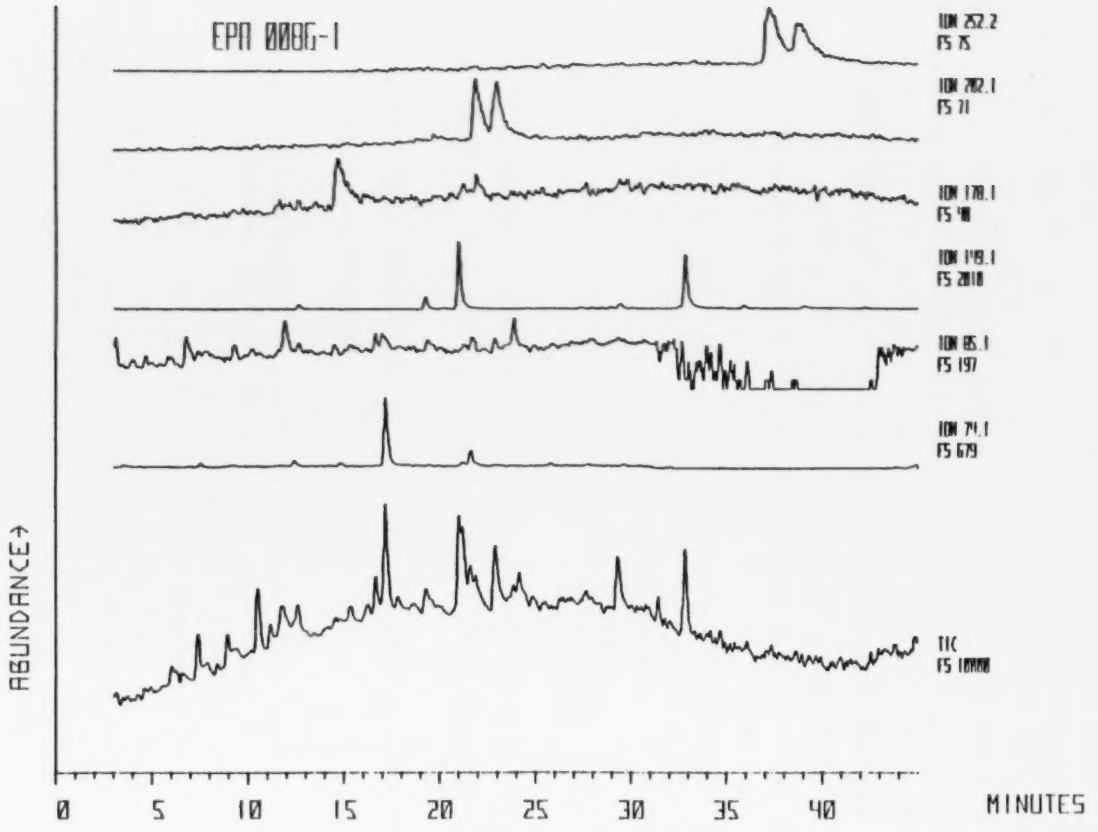


Figure 15. Plots from Dual-Mode analysis of 0082-1

REFERENCES

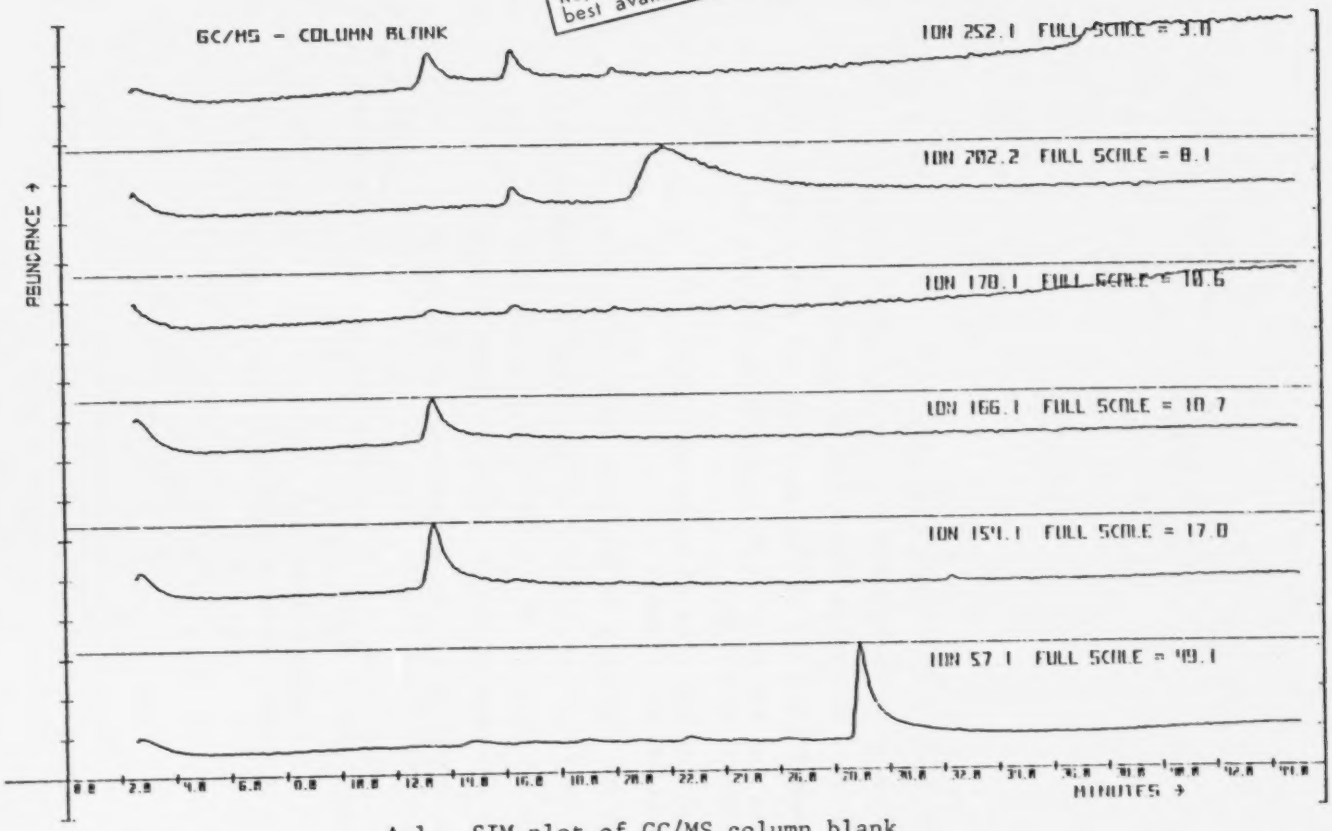
1. G.A. Jutze and K.E. Foster, J.A.P.A., 17, 17 (1967)
2. K.T. Whitby, R.B. Husar and B.Y.H. Liu, J.Colloid Interface Sci., 39, 177 (1972)
3. L. VanVaeck and K. Van Cauwenberghe, Atmos. Environ., 12, 2229 (1978)
4. L. VanVaeck, G. Broddin, W. Cautreels and K. Van Cauwenberghe, Sci. Total Environ., 11, 41 (1979).
5. M. Lippmann and W.B. Harris, Health Phys., 8, 155 (1962)
6. L.J. Forwy, Rev. Sci. Instrum., 47, 1264 (1976)
7. R.K. Stevens, T.G. Dzubay, G. Russwurm and D. Rickel, Atmos. Environ., 17, 55 (1978)
8. T.G. Dzubay, R.K. Stevens and C.M. Peterson in "X-ray Fluorescence Analysis of Environmental Samples," p. 95-105, T.A. Dzubay, Ed., Ann Arbor Science Pub. Inc., Mich., 1977
9. A.R. McFarlard, C.A. Ortiz and R.W. Bertch, Jr., Environ. Sci. Technol., 12, 679 (1978)
10. T.B. Dzubay and R.K. Stevens, Environ. Sci. Technol, 9, 663 (1975)
11. F.W. Karasek, D.W. Denney, K.W. Chan, and R.E. Clement, Anal. Chem., 50, 82 (1978)
12. W.A. Aue and C.R. Hastings, J. of Chromatogr., 89, 369 (1974)
13. H.H. Hill, Jr., K.W. Chan, and F.W. Karasek, J. of Chromatogr., 131, 245 (1977)
14. R.E. Clement, "Application of Computer Techniques to the Collection and Analysis of Analytical Data," M.Sc. Thesis, University of Waterloo, Waterloo, Ontario, August 1976
15. F.W. Karasek, Research/Development, 27, 42 (1976)
16. L.C. Dickson, "Software Improvements for GC/MS/Calculator Used In Trace Organic Analysis of Environmental Samples," Department of Chemistry Report, University of Waterloo, Waterloo, Ontario, April 1979

APPENDIX

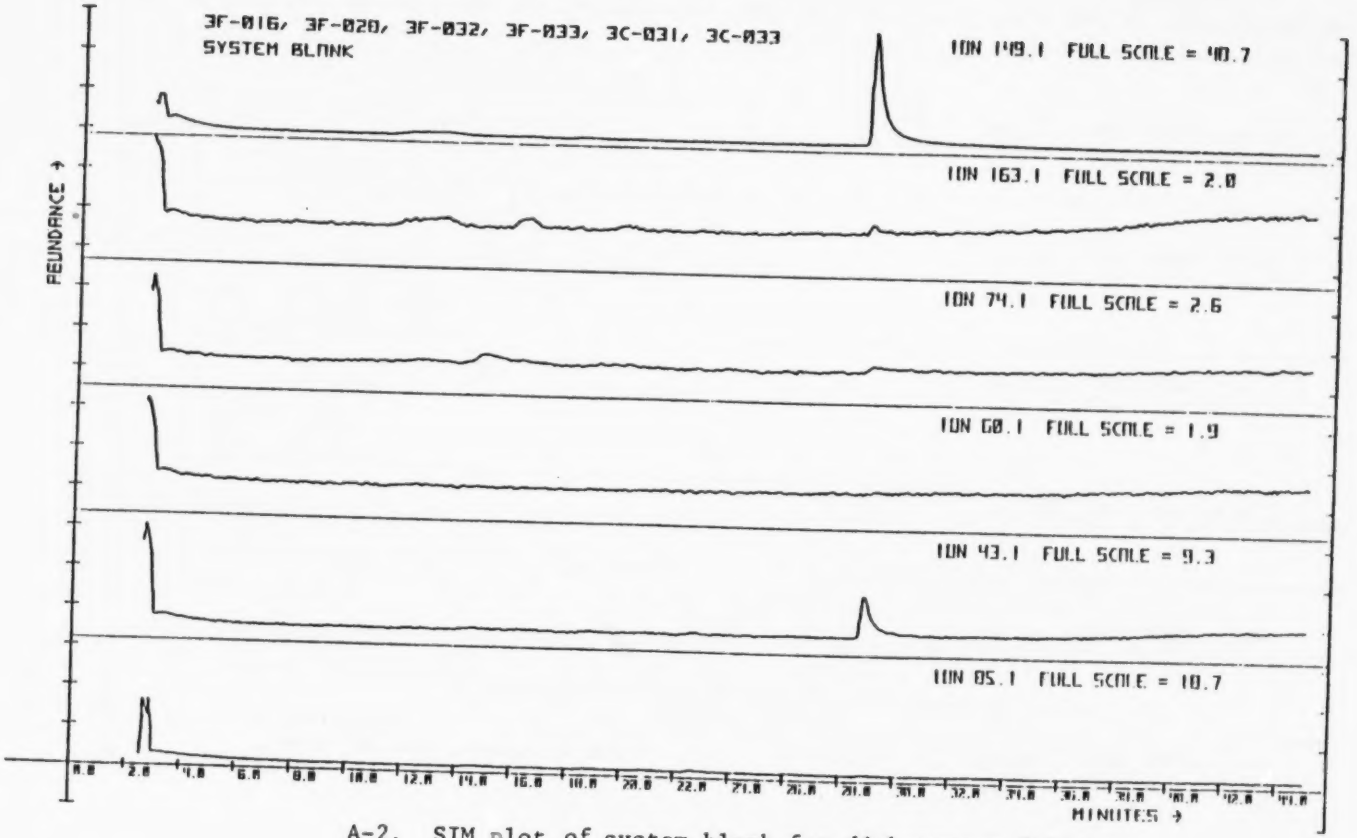
GC/MS DATA

Number		Page
A-1	SIM plot of GC/MS column blank.....	50
A-2	SIM plot of system blank for dichotomous filters.....	51
A-3	SIM plot of system blank for dichotomous filters.....	52
A-3	(Cont.) SIM plot of system blank for dichotomous filters.	53
A-4	Nine ion SIM plot of GC CALIBRATION MIXTURE for dichotomous filters.....	54
A-5	Nine ion SIM plot of instrument blank for dichotomous filters.....	55
A-6	Six ion SIM plot HYDROCARBON STANDARD MIXTURE.....	56
A-6	(Cont.) Six ion SIM plot HYDROCARBON STANDARD MIXTURE....	57
A-7	Six ion plot of GC CALIBRATION STANDARD MIXTURE.....	58
A-8	Six ion plot of METHYL ESTER STANDARD MIXTURE.....	59
A-9	Total ion chromatogram and mass chromatograms of column blank GC/MS.....	60
A-10	Total ion chromatogram and mass chromatograms of Hi-Vol sample 0052-1 GC/MS analysis.....	61
A-11	Total ion chromatogram and mass chromatograms of Hi-Vol sample 0086-1 GC/MS analysis.....	62

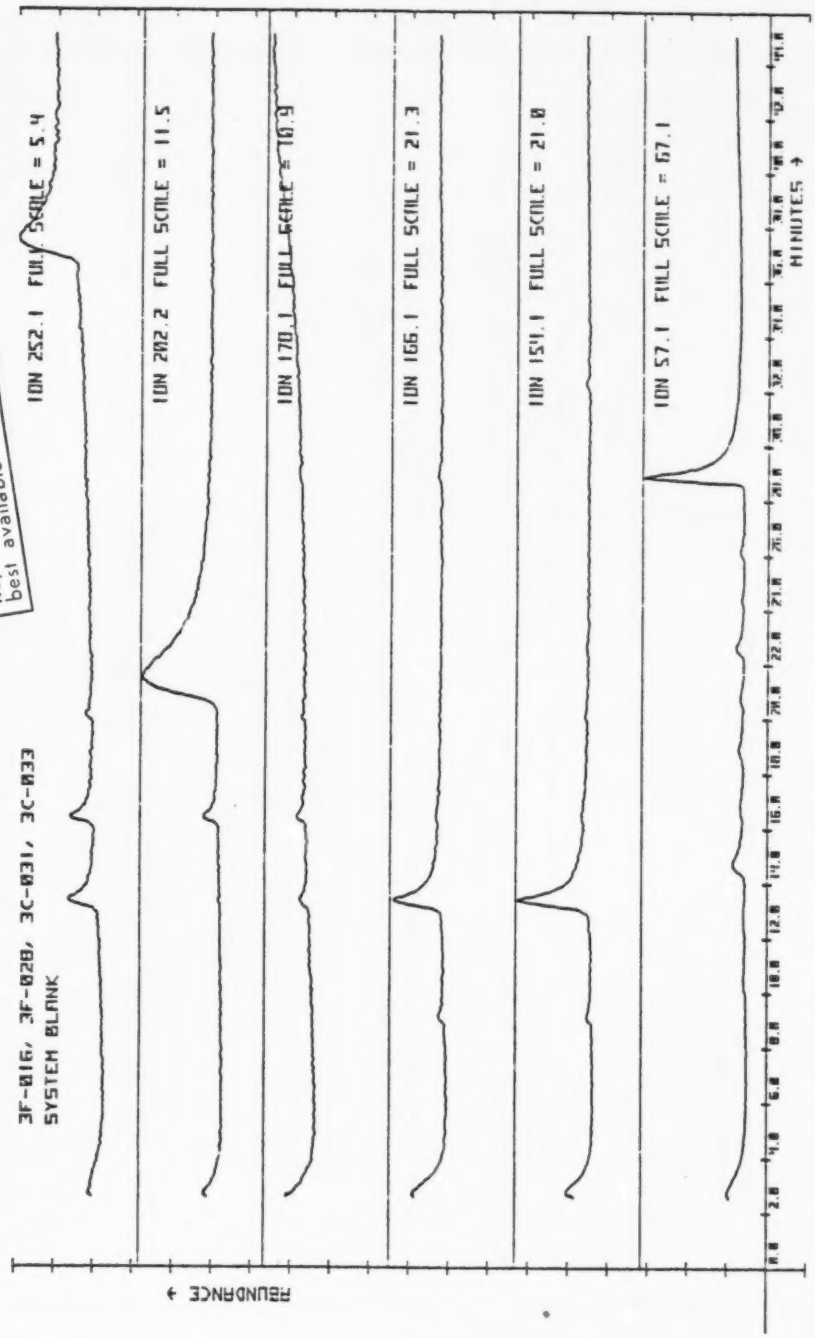
Reproduced from best available copy.


GC/MS - COLUMN BLANK
ION 252.1 FULL SCALE = 3.0
ION 202.2 FULL SCALE = 8.1
ION 178.1 FULL SCALE = 10.6
ION 166.1 FULL SCALE = 10.7
ION 154.1 FULL SCALE = 17.0
ION 57.1 FULL SCALE = 49.1
ABUNDANCE →
MINUTES →

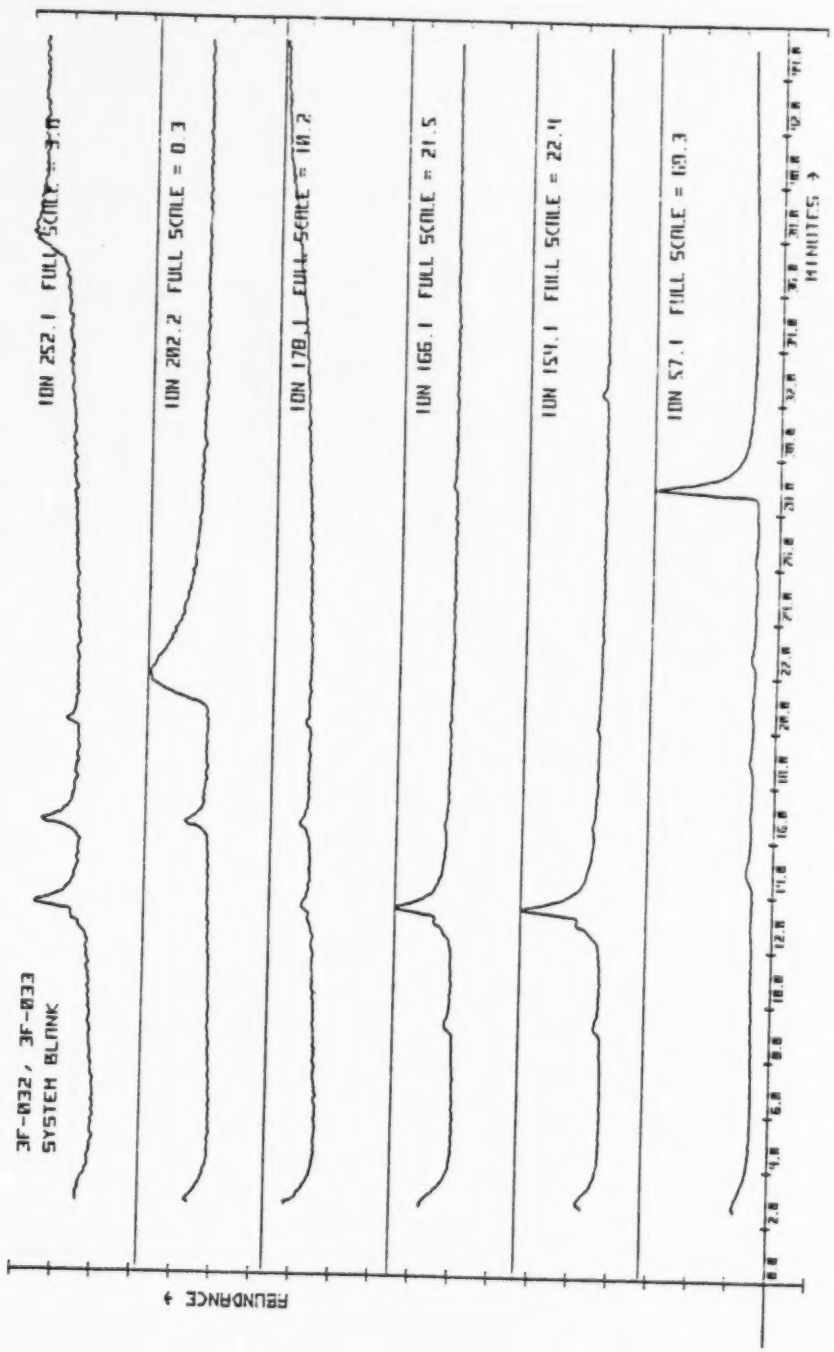
A-1. SIM plot of GC/MS column blank


3F-016, 3F-020, 3F-032, 3F-033, 3C-031, 3C-033
SYSTEM BLANK
ION 149.1 FULL SCALE = 40.7
ION 163.1 FULL SCALE = 2.0
ION 74.1 FULL SCALE = 2.6
ION 60.1 FULL SCALE = 1.9
ION 43.1 FULL SCALE = 9.3
ION 85.1 FULL SCALE = 10.7
ABUNDANCE →
MINUTES →

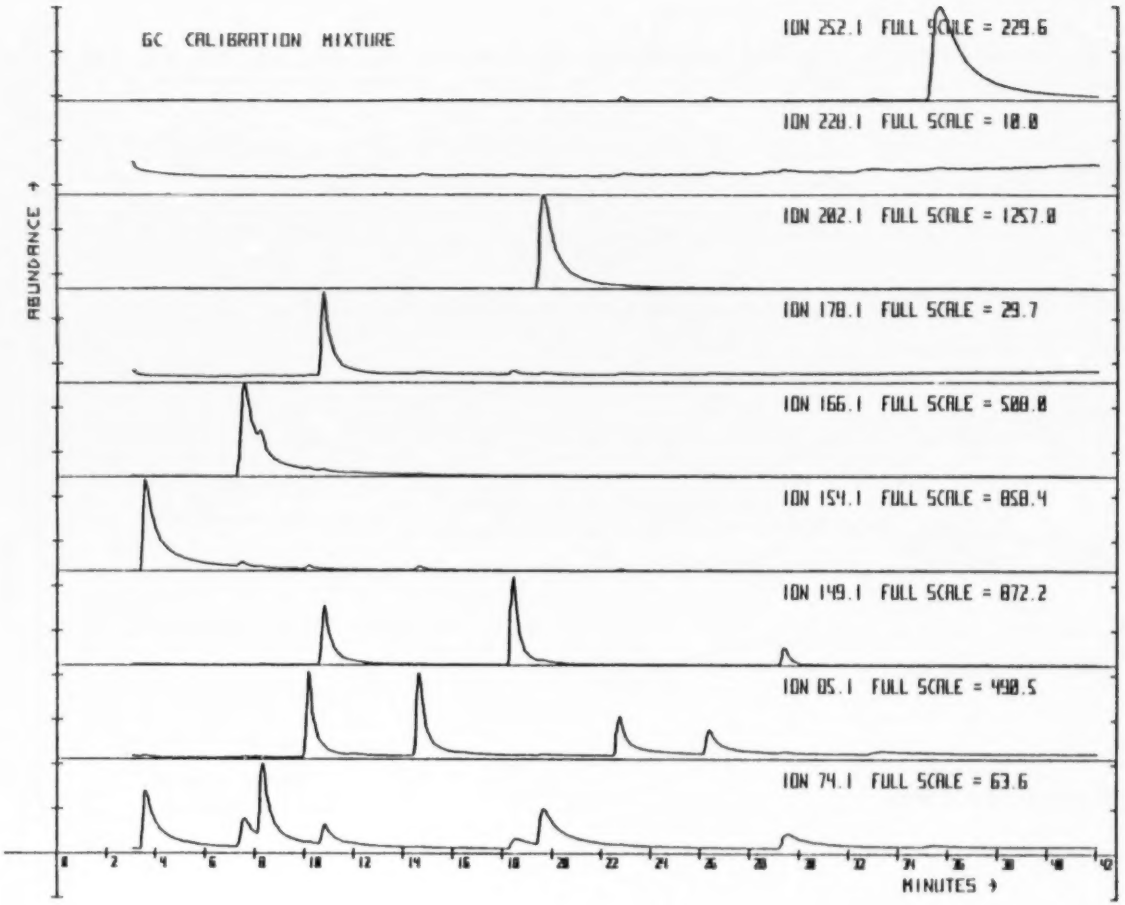
A-2. SIM plot of system blank for dichotomous filters


3F-016, 3F-028, 3C-031, 3C-033
SYSTEM BLANK
ION 252.1 FULL SCALE = 5.4
ION 202.2 FULL SCALE = 11.5
ION 170.1 FULL SCALE = 16.9
ION 166.1 FULL SCALE = 21.3
ION 151.1 FULL SCALE = 21.0
ION 57.1 FULL SCALE = 67.1
ABUNDANCE
MINUTES
Reproduced from best available copy.

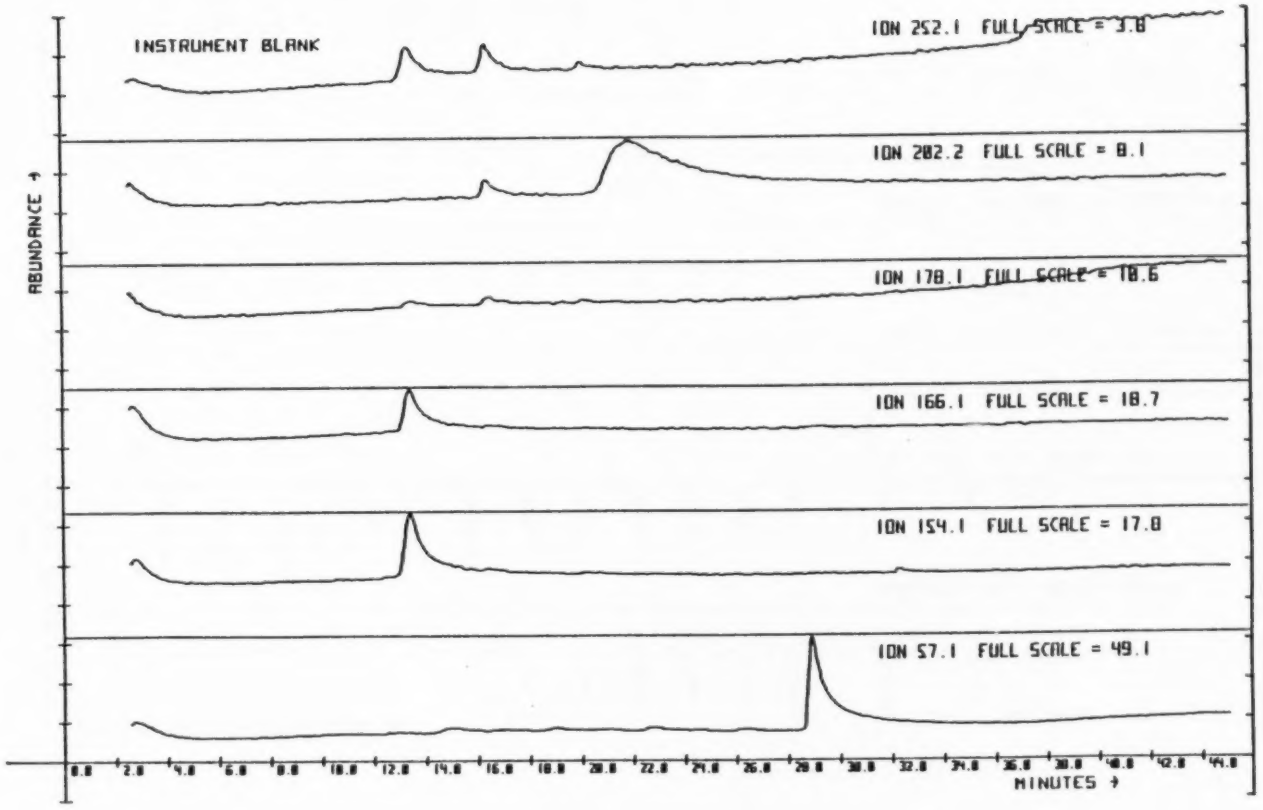
A-3. SIM plot of system blank for dichotomous filters


3F-032, 3F-033
SYSTEM BLANK
ION 252.1 FULL SCALE = 3.0
ION 202.2 FULL SCALE = 0.3
ION 178.1 FULL SCALE = 10.2
ION 166.1 FULL SCALE = 21.5
ION 154.1 FULL SCALE = 22.4
ION 57.1 FULL SCALE = 69.3
ABUNDANCE
MINUTES

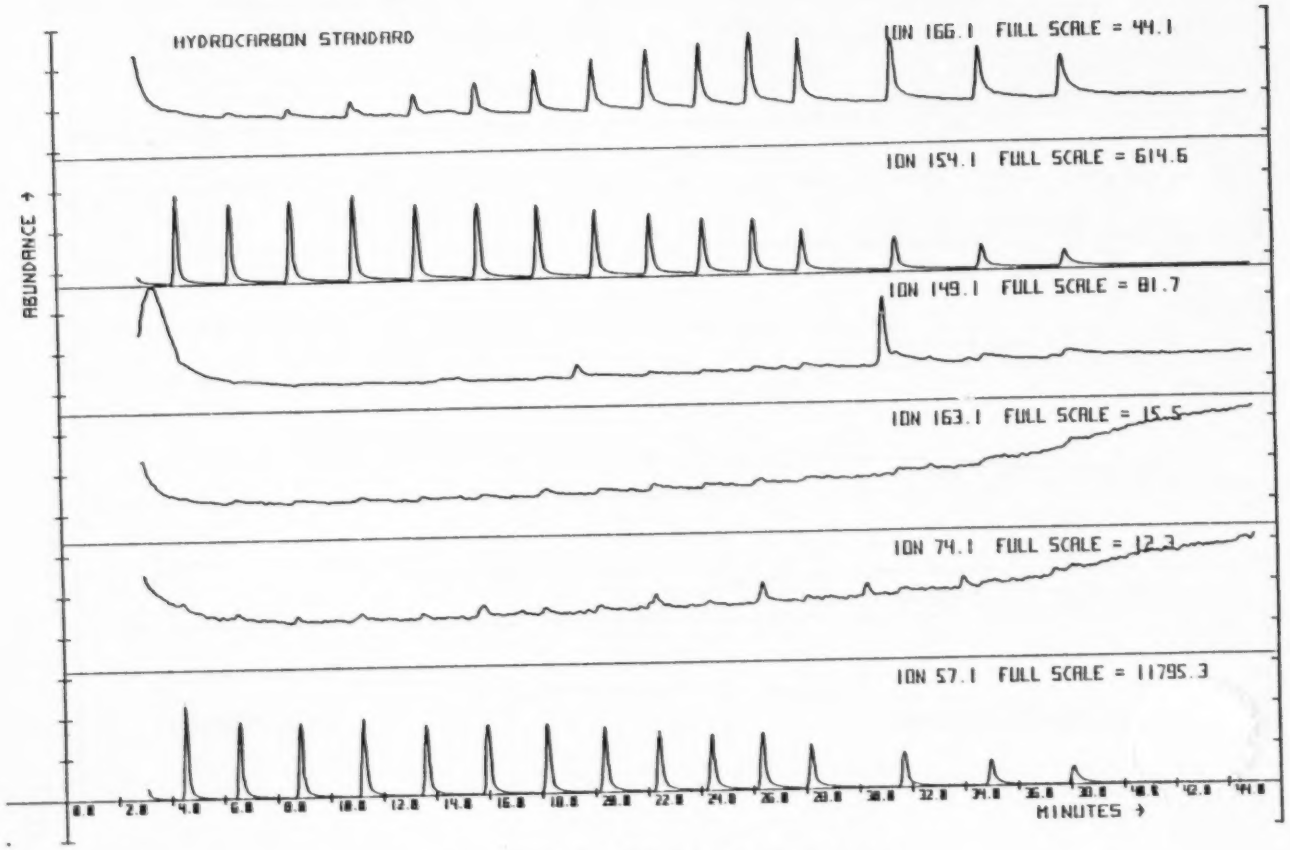
A-3. (Cont.) SIM plot of system blank for dichotomous filters.


GC CALIBRATION MIXTURE
ION 252.1 FULL SCALE = 229.6
ION 220.1 FULL SCALE = 18.8
ION 202.1 FULL SCALE = 1257.8
ION 178.1 FULL SCALE = 29.7
ION 166.1 FULL SCALE = 508.8
ION 154.1 FULL SCALE = 858.4
ION 149.1 FULL SCALE = 872.2
ION 85.1 FULL SCALE = 498.5
ION 74.1 FULL SCALE = 63.6
ABUNDANCE →
MINUTES →

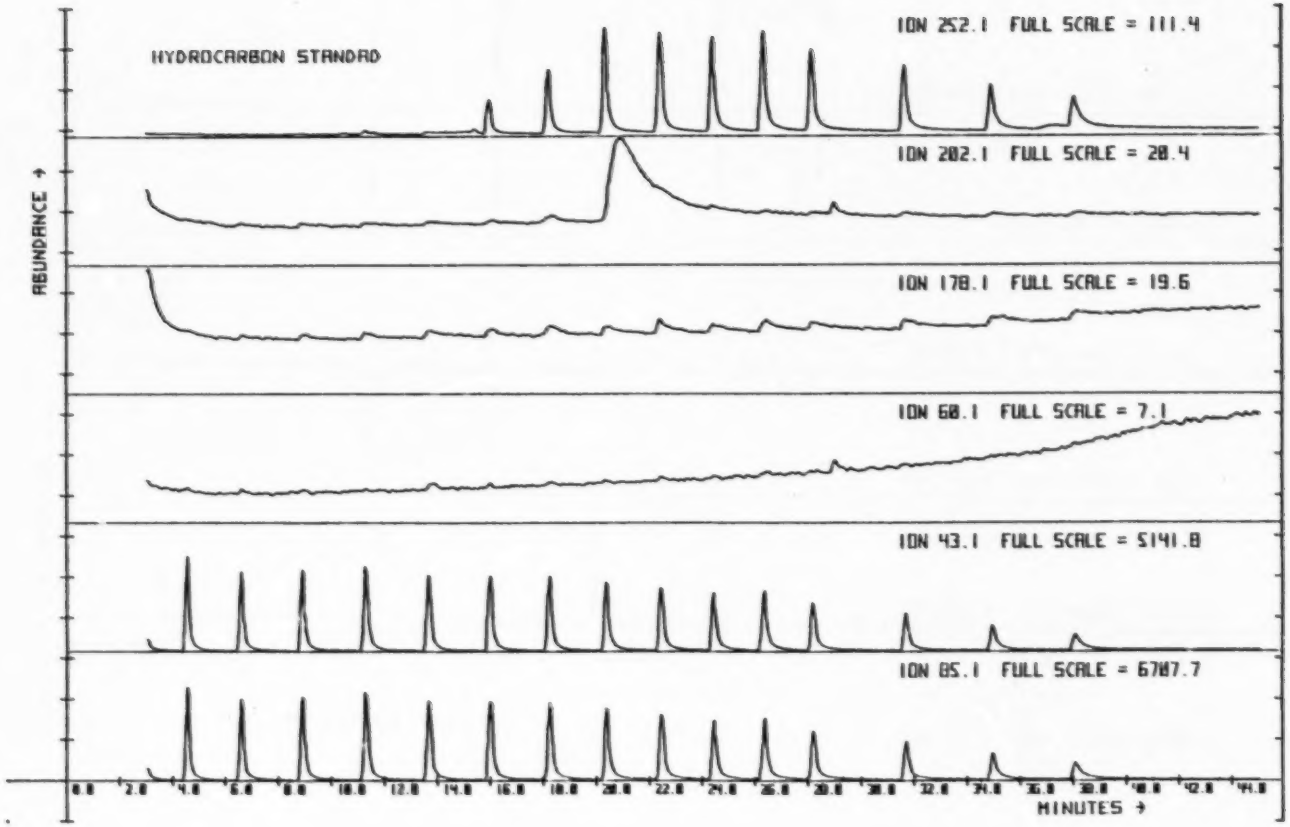
A-4. Nine ion SIM plot of GC CALIBRATION MIXTURE for dichotomous filters


INSTRUMENT BLANK
ION 252.1 FULL SCALE = 3.8
ION 202.2 FULL SCALE = 8.1
ION 178.1 FULL SCALE = 18.6
ION 166.1 FULL SCALE = 18.7
ION 154.1 FULL SCALE = 17.8
ION 57.1 FULL SCALE = 49.1
ABUNDANCE →
MINUTES →

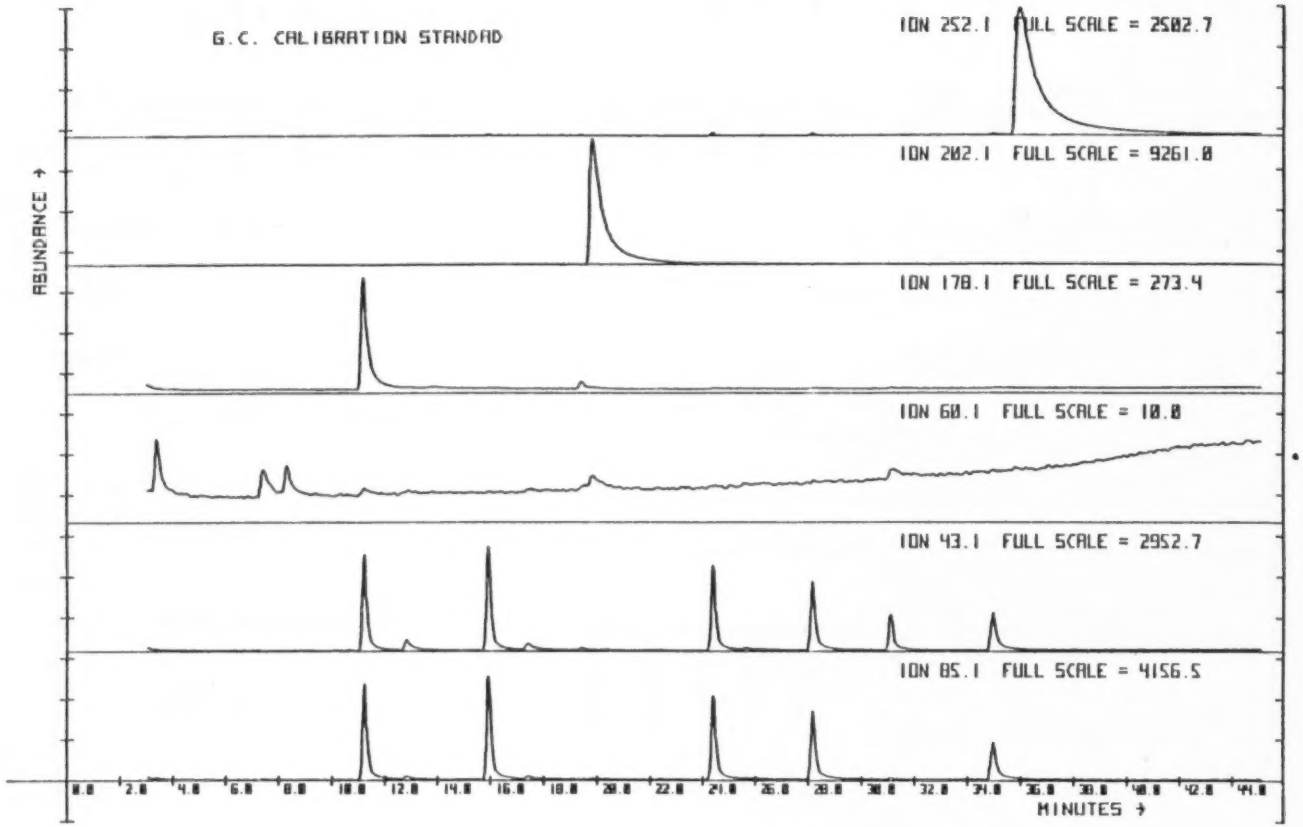
A-5. Nine ion SIM plot of instrument blank for dichotomous filters


HYDROCARBON STANDARD
ION 166.1 FULL SCALE = 44.1
ION 154.1 FULL SCALE = 614.6
ION 149.1 FULL SCALE = 81.7
ION 163.1 FULL SCALE = 15.5
ION 74.1 FULL SCALE = 12.3
ION 57.1 FULL SCALE = 11795.3
ABUNDANCE →
MINUTES →

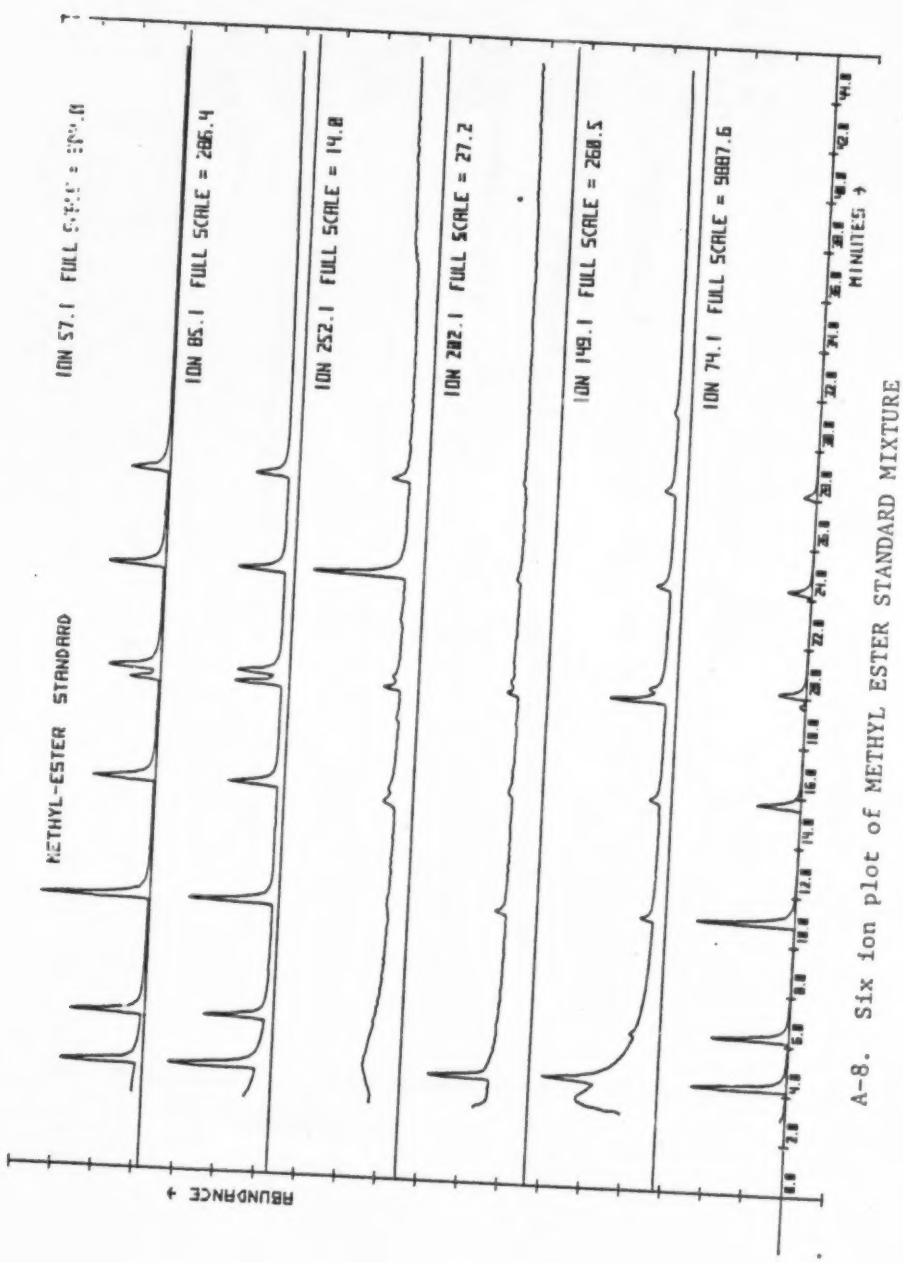
A-6. Six ion SIM plot HYDROCARBON STANDARD MIXTURE


HYDROCARBON STANDRD
ION 252.1 FULL SCALE = 111.4
ION 202.1 FULL SCALE = 28.4
ION 178.1 FULL SCALE = 19.6
ION 68.1 FULL SCALE = 7.1
ION 43.1 FULL SCALE = 5141.8
ION 85.1 FULL SCALE = 6787.7
ABUNDANCE →
MINUTES →

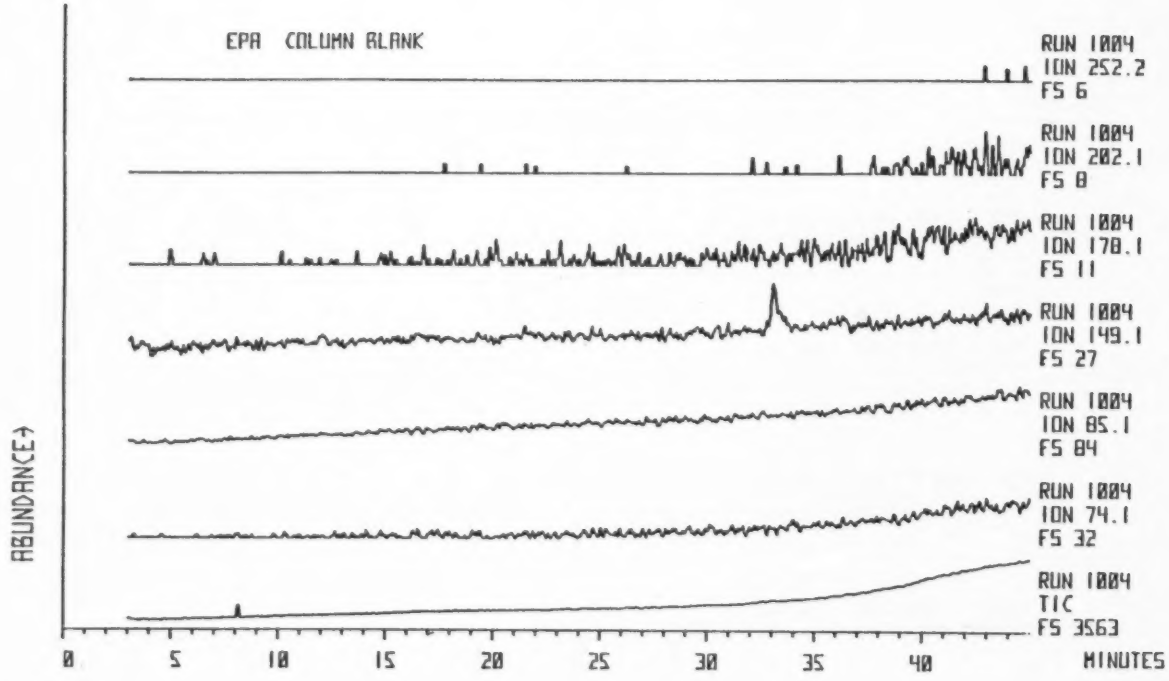
A-6. (Cont.) Six ion SIM plot HYDROCARBON STANDARD MIXTURE


G.C. CALIBRATION STANDARD
ION 252.1 FULL SCALE = 2502.7
ION 202.1 FULL SCALE = 9261.0
ION 178.1 FULL SCALE = 273.4
ION 60.1 FULL SCALE = 10.0
ION 43.1 FULL SCALE = 2952.7
ION 85.1 FULL SCALE = 4156.5
ABUNDANCE →
MINUTES →

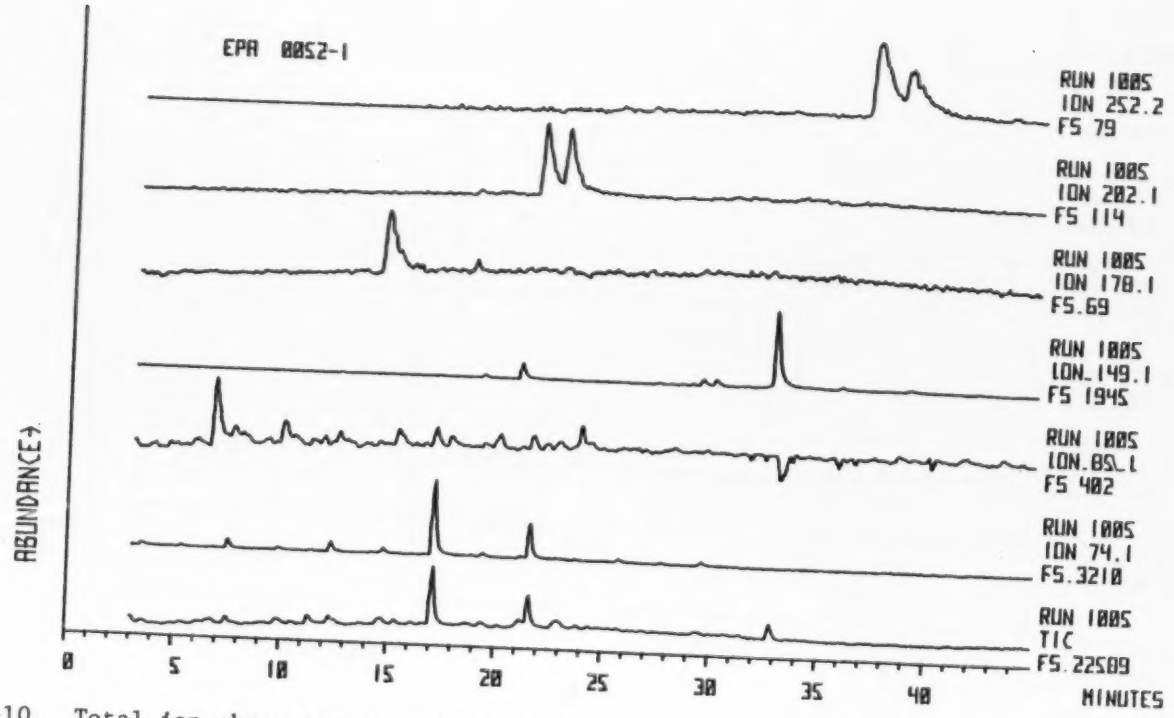
A-7. Six ion plot of GC CALIBRATION STANDARD MIXTURE


METHYL-ESTER STANDARD
ION 57.1 FULL SCALE = 3[illegible].0
ION 85.1 FULL SCALE = 286.4
ION 252.1 FULL SCALE = 14.8
ION 282.1 FULL SCALE = 27.2
ION 143.1 FULL SCALE = 268.5
ION 74.1 FULL SCALE = 9887.6
ABUNDANCE
MINUTES

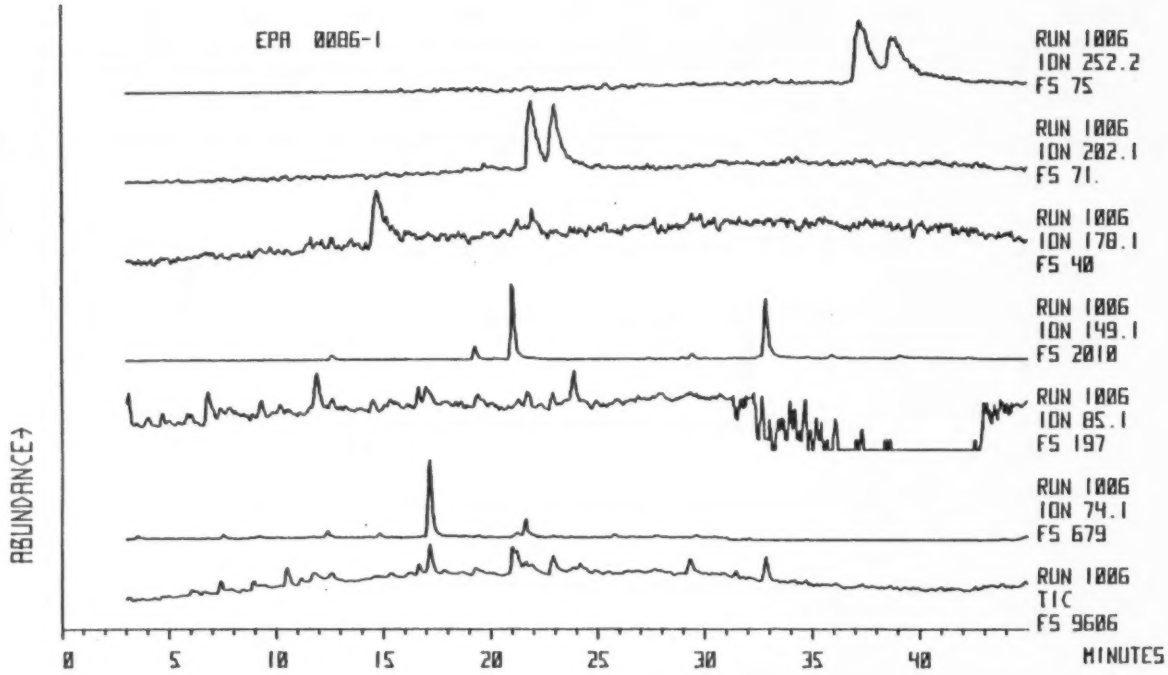
A-8. Six ion plot of METHYL ESTER STANDARD MIXTURE



A-9. Total ion chromatogram and mass chromatograms of column blank GC/MS



A-10. Total ion chromatogram and mass chromatograms of Hi-Vol sample 0052-1 GC/MS analysis



A-11. Total ion chromatogram and mass chromatograms of Hi-Vol sample 0086-1 GC/MS analysis